

PHOTOLUMINESCENCE STUDIES
OF DEEP LEVEL IMPURITIES
IN GALLIUM PHOSPHIDE
AND GALLIUM NITRIDE

HAFLIDI PÉTUR GÍSLASON



DEPARTMENT
OF
SOLID STATE PHYSICS



INSTITUTIONEN FÖR FASTA TILLSTANDETS FYSIK
LUNDS TEKNISKA HÖGSKOLA-LUNDS UNIVERSITET
LUND-SWEDEN

1981



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41553201_0009

PHOTOLUMINESCENCE STUDIES
OF DEEP LEVEL IMPURITIES
IN GALLIUM PHOSPHIDE
AND GALLIUM NITRIDE

HAFLIDI PÉTUR GÍSLASON

PHOTOLUMINESCENCE STUDIES
OF DEEP LEVEL IMPURITIES
IN GALLIUM PHOSPHIDE
AND GALLIUM NITRIDE

HAFLIDI & TÜR GİSLASON



Photoluminescence Studies of Deep Level Impurities in Gallium Phosphide and Gallium Nitride.

by

Haflidi Pétur Gíslason

Department of Solid State Physics, University of Lund,

Box 725, S-220 07 LUND, Sweden

This thesis is based on photoluminescence studies of different impurity centres in two III-V compound semiconductors, GaP and GaN. Optical defect characterization often reveals both the electronic structure of the impurities and their identities. This is the main subject of the thesis, which contains the following scientific reports:

- I Properties of Zn-doped VPE-grown GaN.
 - I. Luminescence data in relation to doping conditions.
J. Appl. Phys. 51, 625 (1980)
- II Properties of Zn-doped VPE-grown GaN.
 - II. Optical cross sections.
J. Appl. Phys. 51, 640 (1980)
- III Optical properties of the Cu-related COL centre in GaP.
Manuscript (1981)
- IV Thermal behaviour of the Cu-related COL bound exciton in GaP.
Manuscript (1981)
- V Neutral defect complexes in GaP doped with Cu and Li.
Manuscript (1981)
- VI Photoluminescence studies of the 1.911 eV Cu-related complex in GaP.
Manuscript (1981)

The author has benefited from the cooperation of Dr. B. Monemar in all papers, Dr. O. Lagerstedt (papers I and II), Dr. P.J. Dean (papers III-IV), Dr. D.C. Herbert (papers III, IV and VI), FK P-O. Holtz (paper IV), Dr. B.C. Cavenett and Dr. S. Depinna (papers V and VI) and Dr. N. Killoran (paper V).

Before turning to the papers, the background for this work will be given and an attempt made to set the subject in perspective. The host materials, GaP and GaN, are discussed and some basic concepts of semiconductor physics briefly reviewed. The techniques of optical defect characterization used in this investigation are described. Also, some common types of optical spectra are discussed. The discussion includes bound exciton spectra, and the powerful tool of bound exciton spectroscopy is illustrated with a few examples.

Lattice vibrations are of vital importance in studying the optical properties of impurities. A fundamental model of coupling between optical transitions and vibrational modes is outlined. Examples of the most important phonon-assisted transitions are given. Finally, the papers are summarized and their results reviewed.

Introduction

GaP and GaN both belong to the family of III-V compound semiconductors. Materials of this family combine controllable semiconductor properties with a wide range of bandgaps [1]. They are therefore an important complement to the classical group IV elemental semiconductors and (as such) are widely used in applications [2]. Many of the good qualities of the group IV materials Si and Ge are at least partly shared by the III-V materials. Thus, some of these have low electrical carrier mass and high carrier mobilities. GaAs is an example of a semiconductor with excellent electrical properties. However, the converse is true for many other III-V compound semiconductors.

Generally, it is more difficult to prepare high quality single crystals of a binary semiconductor than of an elemental one. For many years, crystal preparation was the factor limiting progress towards new applications of compound semiconductors. Many of the problems have now been solved. Well-developed methods of growing bulk material or epitaxial crystal layers in gas phase or liquid phase reactions exist for the phosphides, arsenides and antimonides of aluminium, gallium and indium. It is also possible to form alloys of most pairs of these compounds. Examples are the mixed crystals $\text{Ga}_{1-x}\text{In}_x\text{As}$ and $\text{GaAs}_x\text{P}_{1-x}$. The nitrides, on the other hand, have not been studied much, mainly due to difficulties of crystal growth.

There is considerable interest in many of the III-V compound semiconductors due to the properties which complement those of the group IV materials. In many applications, elemental semiconductors do not possess a sufficiently wide range of useful properties. This is particularly apparent in opto-electronic applications, where the criterion of visible luminescence excludes Si and Ge. For these purposes, semiconductors with energy gaps larger than 1.8 eV are needed. Another goal has been to produce light throughout the entire visible region, which requires bandgaps up to 3 eV. This has turned out to be a difficult task. Besides complicated growth procedures, the electrical properties of large bandgap compounds are often very far from the more ideal behaviour of, e.g. elemental semiconductors [2]. However, maintaining the requirement of visible luminescence, such a comparison of electrical properties is of course unrewarding.

GaP has a bandgap of 2.26 eV at 300 K, which is large enough to allow luminescence in the visible region. It may be prepared as pn junctions, thus

permitting the production of efficient light emitting diodes (LEDs). Most commercial LEDs are made from GaP and the related $\text{GaAs}_{1-x}\text{P}_x$ [3]. In so far as luminescence properties are concerned, gallium phosphide has probably been the most thoroughly investigated of all semiconductors. Many of its extrinsic optical properties are already classified and understood. This is of great advantage when identifying new spectral observations. Academic interest in GaP is due to the fact that radiation can be produced efficiently at room temperature. This is of major interest in LED applications. GaP diodes are excellent emitters of light with energies up to the green region. However, bandgaps above 2.6 eV are needed for blue luminescence.

The interest in GaN is therefore due to its large bandgap, $E_g = 3.44$ eV at 300 K [4]. With proper doping, such a large bandgap allows radiative recombination over a wide range of frequencies. The most serious drawback of GaN is that it is difficult to produce high-quality crystals. The growth parameters depend sensitively on temperature which causes deviations from stoichiometry and a lattice mismatch between epitaxial GaN and the sapphire substrate can induce disorder. Also, undoped GaN is always n-type, with an electron concentration around 10^{18} cm^{-3} , probably caused by native defects such as N vacancies [5]. All attempts to produce low-ohmic p-type material have failed, but compensation can be achieved by doping with acceptors, e.g., Zn. After such doping the material becomes semi-insulating. It is known that Zn-doped GaN is the best available emitter of blue light and that Zn is the most efficient recombination centre in GaN. Unfortunately, the inability to produce p-type GaN controlled by the Zn_{Ga} acceptors is also well established [5,6].

As a consequence of the failure to produce low-ohmic p-type material, pn junctions cannot be made in GaN. However, successful work has been performed on other structures such as the MIS structure [2,7,8]. Here, the insulating I-layer consists of high-ohmic GaN (compensated by, e.g., Zn-doping). Recently, a commercial GaN device emitting blue light of quantum efficiency of about 0.1 % has been announced [9], but no reports are as yet available. Other materials suitable for blue emission include ZnS, $\text{ZnS}_{1-x}\text{Se}_x$ and SiC [10], the last one being commercially available as blue emitting diodes.

General Properties of Gallium Phosphide and Gallium Nitride

I. Gallium Phosphide

Gallium phosphide has the cubic zincblende structure shown in Fig. 1. The Brillouin zone of the zincblende structure is shown in Fig. 2 where the most important symmetry points and lines are also indicated. The bandgap of GaP is indirect as shown in Fig. 3 [11]. The valence band maximum is at the

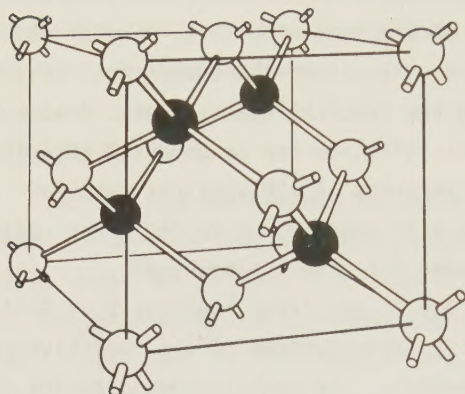


Fig. 1. The zincblende lattice structure. This is the structure of GaP.

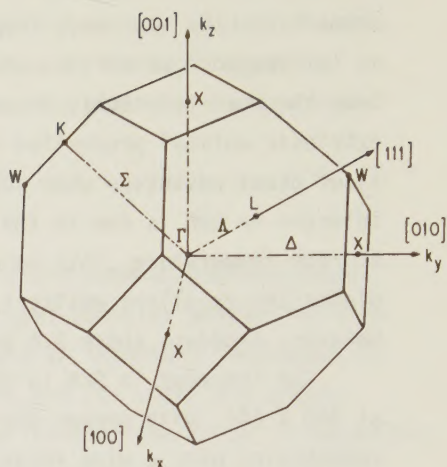


Fig. 2. Brillouin zone for the zincblende lattice. Standard notations are used for the symmetry points and lines.

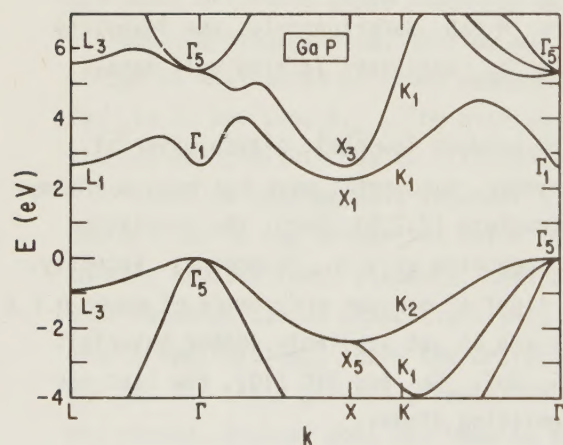


Fig. 3. The energy band structure of GaP. [111].

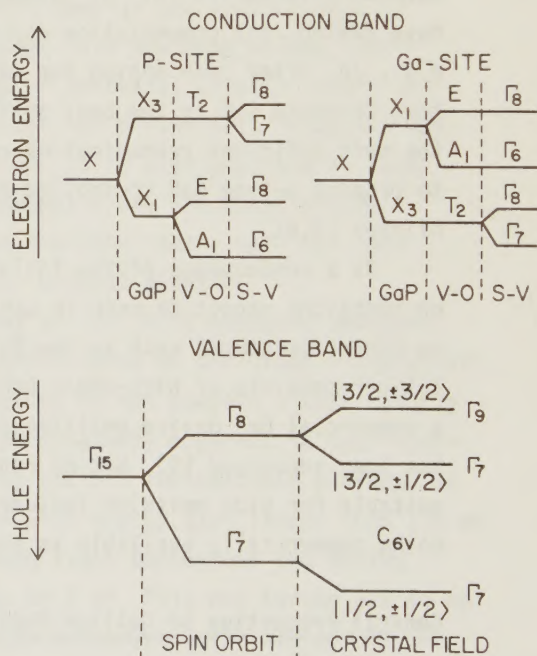


Fig. 4. Electronic structure of bound electron and hole states in GaP. Valley-orbit (V-O) and spin-valley (S-V) splittings are shown for the former [14]. The effect of an axial crystal field along $\langle 111 \rangle$ is shown for the latter.

Γ point where the wavevector $\bar{k} = 0$. The conduction band has its minima near the X points at the zone boundaries in the six $\langle 100 \rangle$ directions. These minima are labelled X_1 in the figure, corresponding to taking the origin at a phosphorus site. The band 0.36 eV higher is labelled X_3 . The order of the labels depends on the choice of origin and they are interchanged if the origin is taken at a gallium site instead [12]. The point group of an impurity at a substitutional site is T_d , the group of the wavevector $\bar{k}$ at the X points is D_{2d} . The X_1 and X_3 minima correspond to the representations A_1 and B_2 of D_{2d} , respectively.

It is now known that the set of conduction band minima in GaP is not exactly at the Brillouin zone boundaries X, but is rather displaced by 8 % of the $\bar{k}(X)$ vector along Δ from the X points. This results in a complicated form of the conduction band structure, referred to as camel's back [13]. The energy of the local maxima of the conduction band at the X points is 3 meV higher than the value at the minima on each side along the $\langle 100 \rangle$ directions. This situation complicates, e.g., the study of excited donor states. Neglecting this effect, there are three equivalent conduction band minima in GaP since the X points at $\bar{k}(X)$ and $-\bar{k}(X)$ differ by a reciprocal vector. For comparison, there are six equivalent minima in Si situated $0.85 \bar{k}(X)$ along the $\langle 100 \rangle$ axes, with a larger splitting $\Delta E = 0.47$ eV [11].

As shown in Fig. 4, the uppermost p-like valence bands Γ_{15} (Γ_5 in Fig. 3) are split by spin-orbit coupling into two components Γ_8 and Γ_7 . The hole functions of the lower energy component Γ_8 transform as the four functions $|3/2, \pm 3/2\rangle$ and $|3/2, \pm 1/2\rangle$ (in the usual $|J, m_J\rangle$ notation). On the other hand, the electron wavefunction derived from the conduction band minima is more complicated because of the several minima involved (Fig. 4). It has been shown that the ground state of a donor at a phosphorus site contains contributions from the three equivalent X_1 minima (neglecting the camel's back structure). The valley-orbit interaction splits this threefold degenerate state into a doublet E and a singlet A_1 in cubic symmetry. The singlet has the lowest energy. Including spin, the representations become Γ_8 and Γ_6 respectively (Fig. 4). For a donor at a gallium site, the ground state is triply degenerate, derived from the X_3 minima. It is not affected by the valley-orbit splitting since the electron wavefunction has a node at the impurity site, but transforms as the T_2 representation of T_d [14].

This difference is reflected in the selection rules for transitions involving these donor states [12]. Since the A_1 state has larger amplitude at the impurity site than the E and T_2 states which have nodes there, the impurity potential can mix the Γ conduction band minimum with the A_1 state. Transitions without phonon assistance are allowed in this case. Thus, the

transition probability is increased for transitions between shallow donor states and the valence band maximum for donors at phosphorus sites. Doping with donors on P sites (as well as isoelectronic impurities) accounts for the fact that this indirect bandgap material can produce efficient extrinsic emission. For donors at gallium sites, the transitions are dominated by phonon-assisted transitions. Here momentum-conserving phonons with wave-vectors at the X minima (e.g., LA^X and TA^X) are involved.

Similar symmetry assignments can be made for interstitial impurities occupying cubic sites [12]. For excitons weakly bound to neutral donors with T_d symmetry, the wavefunctions of the localized particles can be associated with a well-defined wavevector derived from a small part of the vector space. In this case, the selection rules for phonon assisted and phononless transitions mentioned above are valid [12,13]. This is not the case when the exciton wavefunction is extended in the wavevector space through localization of the wavefunction at the impurity site. Coupling to impurity induced localized phonon modes then becomes important.

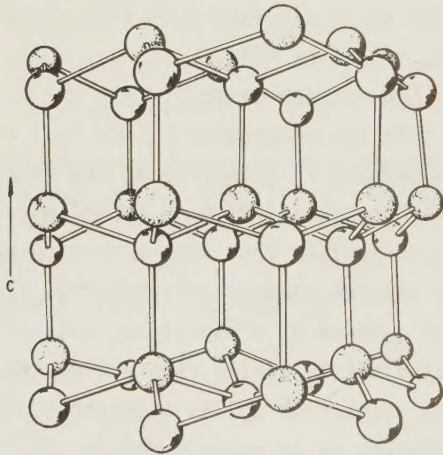


Fig. 5. Hexagonal GaN crystallizes in the wurtzite structure shown here.

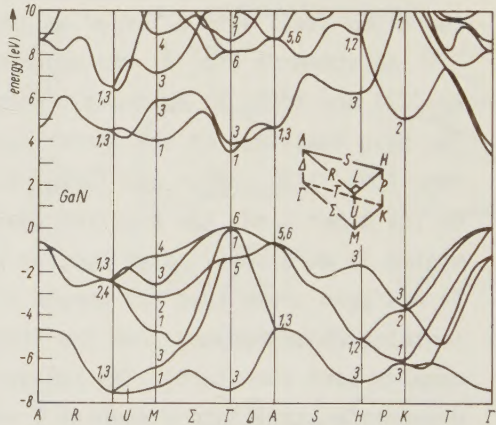


Fig. 6. The energy band structure of GaN. A portion of the Brillouin zone is included.

II. Gallium Nitride

Unlike the lower gap III-V compounds GaN crystallizes in the wurtzite structure shown in Fig. 5. The orientation of the epitaxial layers depends on the crystallographic orientation of the substrate. Usually, a [0001]-oriented sapphire substrate is used. This is, however, not the ideal substrate material for GaN. Sapphire has a rhombohedral structure, which can

only approximately be described as a hexagonal system. This gives a lattice mismatch of 14 % between GaN and the substrate, resulting in a high density of dislocations near the substrate. In addition these materials have rather different thermal expansion coefficients, which induces large stresses in the samples upon cooling down from the growth temperature. In spite of these difficulties, sapphire is the best of the substrate materials hitherto used for the epitaxial growth of GaN [15,16].

As is shown in Fig. 6, the large bandgap (3.5 eV at 0 K) is direct. A portion of the Brillouin zone is included in the figure with the most important high-symmetry points labelled [17]. The band structure has been calculated by an empirical pseudopotential method. The same pseudopotential as for ZnO is used, since these two wurtzite materials have almost equal lattice constants [17,18]. As is usual in hexagonal crystals, the phonon dispersion curves are difficult to obtain, and these are not available for GaN. From polarized reflection spectra, the LO phonon energies have been reported to be 95.4 (E || c-axis) and 99.2 meV (E $\perp$ c-axis) [19]. The TO energies are 66 (A_1) and 69 (E_1) meV [19] as determined by Raman spectroscopy. The representations in parentheses correspond to the C_{6v} point group of hexagonal GaN.

Impurities in Semiconductors

Some basic concepts

The concept semiconductor is based on the classification of solids into three groups in terms of their electrical properties as conductors, semiconductors and insulators. The intrinsic properties of conductors and insulators make them directly applicable for practical purposes. On the other hand, the enormous importance of semiconductors depends on extrinsic properties attained by the incorporation of impurities.

The energy levels of electrons in perfect crystals form a series of bands separated by gaps. All materials have core bands which correspond to the energy states of the atomic core and are occupied by electrons. In metals, these bands are followed by a set of partly occupied bands. In semiconductors and insulators, the core bands are followed by the completely filled valence bands (at 0 °K), the fundamental energy gap and finally the empty conduction bands (at 0 °K). At absolute zero, a semiconductor becomes an insulator. In a perfect crystal, the electronic states must satisfy the periodic boundary conditions. The wavefunctions of all states have the same probability amplitude in each unit cell of the crystal. Localized states can only appear if the periodicity is broken, e.g., if the crystal contains point

defects such as impurities. Such states are introduced into the otherwise forbidden bandgap and the presence of these states governs the properties of the semiconductors.

Depending on whether or not it is occupied, an impurity can exist in different charge states. Schockley has given a definition of donors and acceptors in these terms: "Positively charged states of an impurity are defined as donor states, and negatively charged states are defined as acceptor states" [20]. Impurities replacing a host atom from the same column of the periodic table are usually referred to as isoelectronic in the sense that they have the same number of valence electrons per unit cell. Substitutional impurities with higher chemical valence are generally called donors, whereas substitutional impurities with lower chemical valence, which have to accept electrons from host atoms to satisfy local bondings, are referred to as acceptors.

With the exception of some isoelectronic impurities, all point defects seem to give localized states in the bandgap of the host semiconductor [21,22]. The localization of the states is often such that a large portion of the electronic charge is outside the deep atomic potential of the defect. The one-electron approximation thus becomes a suitable starting point. The problem of solving the one-electron Schrödinger equation is generally that of solving:

$$H\Psi = E\Psi \quad (1)$$

where

$$H = H_0 + V(\vec{r}).$$

Here, H_0 is the perfect crystal Hamiltonian and $V(\vec{r})$ an impurity potential at the site of the point defect. Impurity levels can be classified as shallow or deep states depending on the localization of the states they introduce into the bandgap. If the wavefunction is considerably delocalized, the details of $V(\vec{r})$ and the electron-lattice interaction can be treated as a perturbation.

The simple case when the boundary conditions at small $\vec{r}$ are of little importance leads to the hydrogenic or effective mass equation [23], the localized states in the gap then resembling the spectrum of a hydrogen atom. The host material is characterized by its static dielectric constant. The overall behaviour of shallow donors and acceptors is quite well described in terms of the hydrogenic model. However, in most cases, the electron wave function interacts with the impurity and the properties of the impurity and host crystal must be treated on an equal footing. This is most obvious for the lowest s-like states of the electron wavefunction which are symmetric around the impurity sites.

When the wave function $\Psi(\vec{r})$ becomes more localized, the electron wavefunctions of the localized states are increasingly sensitive to the impurity structure. The increasing importance of a short-range term in the impurity potential $V(\vec{r})$ summarizes the deep level problem. For strongly localized wavefunctions, local effects dominate the Hamiltonian. To find a solution of the deep-level Schrödinger equation is a many-particle problem with both long-range Coulombic terms and short-range interactions [21,22].

The role of impurities in semiconductors depends on the kind of energy levels they introduce into the bandgaps and on other impurities which are present simultaneously. The significance of shallow impurities arises from their role in controlling conductivity. By varying their concentrations, a wide range of conductivities can be obtained. This controlled doping, n-type or p-type, respectively, is exploited in semiconductor devices of all kinds. A few examples are pn junctions and other diodes, emitters of radiation such as LEDs and laser diodes. The list can be made long.

Deep level impurities play a very different role. Their most important function is to control the lifetime of carriers [24]. This they do by providing an energy level around the middle of the bandgap. Recombination is most efficient when this level has a series of excited states, enabling the electron to recombine through a cascade process [25]. Deep impurities can generally be incorporated into crystals in smaller concentrations than the shallow ones. In applications where the carrier lifetime is important, controlled doping with deep level impurities is critical. In, e.g., photocells, deep impurities must be avoided to ensure maximal lifetime of the carriers, whereas in fast switches the converse is true.

Isoelectronic impurities are not covered by the above discussion of shallow and deep impurity states. These are neutral without capturing an electron or a hole, as is typical for substitutional atoms of the same column as the host atom replaced. The wavefunction of an isoelectronic impurity consists of a bound exciton wavefunction, which can be looked upon as constructed of band wavefunctions from large regions of k-space. Because of the short-range forces by which isoelectronic impurities bind excitons, they can cause an overlap between the electron and hole wavefunctions from different points in k-space. Thus, an effective radiative recombination can be produced even in materials with indirect bandgaps. An example of this is the well-known case of N in GaP [2,26]. I shall return later to isoelectronic impurities.

Optical Defect Characterization

Photoluminescence measurements and related techniques are of great advantage in identifying recombination processes and defect characterization when

the energy supplied by excitation is released in the form of radiation. The various experimental techniques used in this work are based on photoluminescence measurements:

Photoluminescence emission measurements. The emission from an optically excited sample is analysed spectrally. These measurements can be performed at different temperatures (typically 1.6 K - 300 K) and with varying excitation intensities.

Photoluminescence excitation (PLE) measurements. A portion of an emission spectrum is selectively monitored, either broad-band with a filter or through a monochromator with selectable bandwidth. The spectral dependence of the excitation process is measured by varying the excitation wavelength. This method has been greatly improved by the advent of tunable dye lasers, which provide high intensity combined with small bandwidth. The PLE technique allows measurements of transitions with very small oscillator strengths and has been found to be very powerful.

Zeeman measurements. The photoluminescence techniques mentioned above can be performed in a strong magnetic field in order to reveal the magnetic degeneracy of the energy levels under study. By rotating the direction of the field, information about defect symmetry is often obtained.

Optically detected magnetic resonance (ODMR). This method combines a magnetic field and a microwave oscillator field, which induces transitions between decomposed energy levels split by the magnetic field. In proper conditions, this method is an extremely sensitive way of measuring defect symmetry. By monitoring the characteristic photoluminescence emissions of a certain defect, variations in intensity as a function of the magnetic field at a certain microwave frequency are recorded. In addition resonance signal can be spectrally analysed in order to relate it to the defect.

Types of Optical Spectra

One of the most common types of emission spectra observed is pair emission. Ever since pair spectra were first recognized, they have given very detailed information about binding energies and the interactions between impurities [6]. Pair emission occurs when electrons at neutral donor sites recombine with holes at neutral acceptor sites. An electronic dipole from the ionized centers is created as a result of the recombination, contributing energy to the emitted photon. If the binding energy for the particles is sufficient for the centres to be relatively localized, the spectrum for the closer pairs breaks up in discrete lines, corresponding to different pair separation. The energy released when donor electrons

recombine with acceptor holes is

$$F = F_0 - F_1 - F_2 + \frac{e^2}{R} + f(R) \quad (2)$$

The term $f(R)$ is composed of contributions from initial state interactions. It vanishes for large pair separations R [29,30].

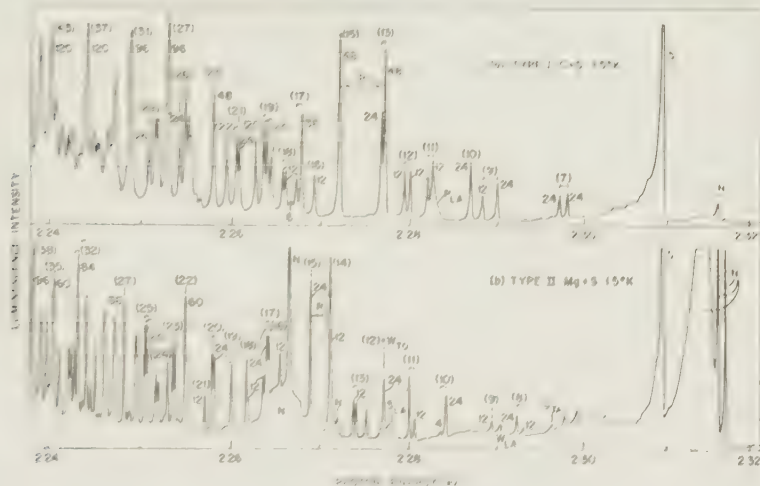


Fig. 7. Two typical shallow donor-acceptor pair spectra in GaP. The discrete pair separations R are denoted by shell numbers in parentheses [31].

Detailed calculations of the sum of the donor and acceptor energies $E_D + E_A$ have been made for GaP. Thus, many donor or acceptor ionization energies relative to E_g have been determined, given one value independently. Representative spectra for two pairs of impurities are shown in Fig. 7. The donors and acceptors are on similar (I) and opposite (II) lattice sites [31]. In contrast to GaP, semiconductors such as GaAs and InP with narrower direct bandgaps have low values of the sum $E_D + E_A$. Discrete donor - acceptor pairs have not been resolved in these materials. However, distant-pair peaks are distinguished and luminescence bands from transitions between free electrons and bound holes can be seen. This has been used to identify shallow acceptors in GaAs and InP [2].

Tunable dye lasers have made possible a method for measuring the excited states of acceptors directly, by selecting a particular pair line and measuring its intensity as a function of laser excitation. When the excitation energy coincides with the energy separation between the donor ground state and an excited state of the acceptor, a resonance effect is

observed as an intensity peak [32]. Both s-like and p-like excited states can be detected in this way, since dipole selection rules do not govern transitions between different centres.

A quite different problem generally occurs with deep level impurities in optical absorption and luminescence. Luminescence involving a shallow donor or acceptor usually exhibits a dominant zero-phonon line with phonon replicas characteristic of the host material. As the localization of the particle wavefunction increases, the coupling to defect-induced phonons also increases. In the limit of a highly localized state, the major part of the emission is phonon-assisted. The line-shapes of absorption and emission spectra then depend on both electronic energy and phonon coupling. This gives sidebands extending well above zero phonon energy in absorption and the opposite in emission. The coupling strength is also temperature dependent. To deduce the binding energy for deep levels from purely optical measurements, the contributions of the electronic transition and the vibrational coupling have to be separated. This has been accomplished for the electronic cross-section in transitions between the deep 0 donor in GaP and the band states, as well as for the pair recombination between the 0 donor and the shallow C acceptor in GaP, as an example [33].

As a consequence of strong coupling to lattice vibrations, most transitions involving deep levels are non-radiative. Only in a few cases has information on electronic states and phonon interaction been obtained from photoluminescence studies or other related techniques. Some well-known examples involving 0 are the Zn-0 and Cd-0 nearest neighbour pairs in GaP [34-35], which are neutral but can bind an electron tightly. The electron can recombine with a shallow acceptor giving red emission. Since the complex is neutral after recombination, there is no Coulomb interaction between the impurity pair as in pair emission. The dominating radiative recombination connected with Zn-0 and Cd-0 is, however, the bound exciton decay [3].

Additional complications arise when the impurities are not from the main groups of the periodic table, which have closed-shell core configurations. Examples of this occur when transition series elements are used as substitutional impurities. These produce deep states for which an effective mass description is totally inappropriate. Often internal transitions between two such atomic states are observed, sometimes radiative. These are observable usually only in wide-bandgap host materials. Examples of impurities with open-shell configurations are Cu_{Zn} in ZnO, which shows a high energy luminescence band associated with $\text{Cu}^{++}(3d^9)$ [37], and Cr_{Ga} in GaAs, which gives rise to near infrared luminescence attributed to transitions at $\text{Cr}^{++}(3d^4)$ [38]. Luminescence at transition metal centres has recently been reviewed [39].

Excitons

An exciton is a neutral excitation of a crystal which is invariant with respect to the translational symmetry of the crystal. There are two extreme forms of exciton states, which were described already 50 years ago. The very localized Frenkel exciton is an excited electron describing an orbit of atomic dimensions around an atom with a vacant valence state. In the lowest approximation, the low-lying excitations are the excited states of the individual molecules [40]. In the Wannier-Mott picture, the free electron and free hole are weakly coupled by their Coulomb interaction, but separated by many lattice distances [41,42]. While the Frenkel picture is appropriate for some ionic crystals such as the alkali halides, the Wannier model of the free exciton is applicable to Group IV semiconductors and many others of partial covalent character, e.g., III-V compounds.

The term exciton has been extended to include the excitation of an impurity when its basis functions contain to a good approximation free electron and hole functions. Such bound exciton states were first predicted in 1958 [43]. Shortly later, appropriate experimental techniques to demonstrate bound excitons in semiconductor material of high quality were developed. Since the first evidence was obtained [44], bound exciton spectroscopy has developed rapidly. Some highlights are the identification of isoelectronic traps of the single substitutional type [45] and the molecular donor-acceptor associate type [34,35], two particle transitions [46], bound phonon effects [47] and multiple bound excitons [48]. A review of bound excitons (BE) in semiconductors, where these phenomena are discussed, has recently been published [13].

Exciton binding energy

Before turning to some cases of excitons binding to isoelectronic traps, the general mechanism of which is still incompletely understood, a few results for the case of donors and acceptors will be mentioned. The simplest bound exciton system consists of an electron-hole pair bound to an ionized donor or acceptor. Only two particles are present in the excited state and effective-mass theory with various correction terms provides good qualitative approximations in many cases. Only very shallow bound exciton states for binding at ionized impurity levels are possible. There exists a critical mass ratio for the effective masses of the electrons and holes, respectively, above which the bound complex is unstable. For ionized donors, it is necessary that $m_h^* \gg m_e^*$. If instead $m_e^* \gg m_h^*$, the hole wavefunction is very delocalized from the neutral donor and the kinetic energy required to localize the hole exceeds the corresponding gain in potential energy. The mass ratio must be

inverted for exciton binding at ionized acceptors [13].

It was at an early stage postulated that a bound exciton complex can always bind at neutral centres [49]. Several theoretical treatments of this system have been made. These show large discrepancies between different calculations of the exciton localization energy as a function of the mass ratio m_e^*/m_h^* . Experiments seem to support the calculations which predict that all mass ratios give stable complexes with a maximum binding energy for $m_e^*/m_h^* \approx 1$ [13]. Numerous examples of excitons bound to neutral donors and acceptors have also been observed. Transition metal impurities with an open d-shell are an exception in some cases. Hole-hole repulsion between the BE hole and the d-hole states of the impurity may prevent the binding of an exciton to a neutral acceptor. This is thought to make a BE state unstable, e.g., for GaAs:Mn [50], where the neutral acceptors have an incomplete d-shell.

For neutral donors and acceptors dominated by the Coulomb attraction, the exciton binding energy E_{BX} can often be described as a linear variation with increasing impurity binding energy E_i :

$$E_{BX} = a + bE_i.$$

This is known as the generalized Haynes' Rule [13]. The behaviour observed is often remarkably linear, even when there are substantial central cell corrections. For Si, the parameters are $a = 0$ and $b = 1$. In GaP, the line does not pass through the origin and a is different for acceptors and donors. The form of E_{BX} as a function of E_i has not as yet been determined for many semiconductors. For low bandgap materials, differences in binding energies may be too small to permit reliable detection of changes in E_{BX} . However, it has been established that E_{BX} depends only weakly on E_A for shallow acceptors in some direct bandgap semiconductors such as InTe or GaAs and InP [13]. In a few cases such as InP:Zn and InP:Cd, the energies do not even increase together.

A precise method for determining acceptor binding energies is the use of two-hole BE satellites. These are observed as transitions to excited states of the neutral acceptors to which the excitons are bound upon BE recombination. The energy difference between the two-hole satellite and the BE ground state is equal to the energy shift of the excited state relative to the ground state. Many shallow acceptors in GaAs and InP have been identified in this way. However, shallow donors in these materials have a narrow total range of chemical shift (about 0.1 meV). Therefore, even this method has too poor resolution [2]. In GaP, the corresponding acceptor-bound excitons are weak and the phonon-assisted transitions strong, so that two-hole satellites are not detectable. Two-electron spectra, however, have been observed for the shallow donors and used

to obtain donor binding-energies in GaP [13,46]. Transitions of a two-particle character reveal excited states with even parity, whereas those reached by infrared absorption have odd parity.

Excitons bound to isoelectronic impurities

Isoelectronic impurities were first identified in 1965 [45]. They were initially thought to bind electrons and holes only in pairs, as excitons. Later, it was proposed that the binding may be viewed in two steps. First, one of the particles is bound, whereby the impurity becomes charged. The second particle is then trapped by the resulting Coulomb field. This is the so called Hopfield-Thomas-Lynch model (HTL model) [51]. According to this model, the electronegativity of the impurity determines whether a particle is bound at the neutral impurity, and also whether it is an electron or a hole.

Despite agreement with observations in some cases, the electronegativity rule is generally insufficient to predict those systems which actually have bound states. Rather, it is now realized that the binding energy can be very sensitive to both the strength of the impurity potential and to lattice distortions [22]. The binding of an exciton to an isoelectronic defect is a finely balanced phenomenon. Lattice distortion may therefore be a determining factor. In spite of a vast amount of experimental work on isoelectronic impurities and much theoretical effort to explain the binding mechanism, no numerically convergent calculations for isoelectronic impurities have been reported [21,22]. According to the HTL model, isoelectronic impurities can be classified as isoelectronic donors and acceptors. If the electron is most tightly bound and the hole is bound by the Coulomb field of the electron, the situation is very effective-mass-like. This has been demonstrated clearly for excitons bound to NN pairs in GaP, where several s-like excited hole states have been observed for the hole [57].

The reason for the current interest in isoelectronic centres is their role in radiative recombinations. They give rise to the possibility of tightly bound states where no concurring irradiative Auger process can occur, since only two electronic particles are involved. The isoelectronic centre is the only defect centre in semiconductors known to be able to bind excitons tightly while still producing efficient radiative recombination. Most experimental work on excitons bound to isoelectronic impurities has been carried out using GaP. The main part of this thesis also concerns isoelectronic complexes in this material.

Several examples of isoelectronic traps in GaP have already been mentioned. N_p , NN pairs and $Zn_{Ga}-O_p$ illustrate well the different forms in which these

traps occur. The luminescence spectra of excitons bound to isolated N atoms and NN pairs in GaP are shown in Fig. 8 [45]. Besides single substitutional types and molecular pairs of simple donors and acceptors, there are more complex types such as $\text{Li}_{\text{Ga}}\text{-Li}_{\text{I}}\text{-O}_{\text{P}}$ [53]. Neutral transition metal impurities bind excitons which suffer hybridization with the d-core states. Also, we may include complexes of substitutional and interstitial species. Such defects involving Cu in GaP define a distinguishable class of isoelectronic complexes, as discussed in the papers.

Thanks to comprehensive luminescence studies, nitrogen in GaP is one of the best known simple substitutional isoelectronic impurities [3,13]. From absorption and luminescence spectra it is known that nitrogen binds an exciton (Fig. 8). The phonon-assisted transitions are much stronger (by an order of magnitude) than is found for excitons bound to neutral P-site donors.

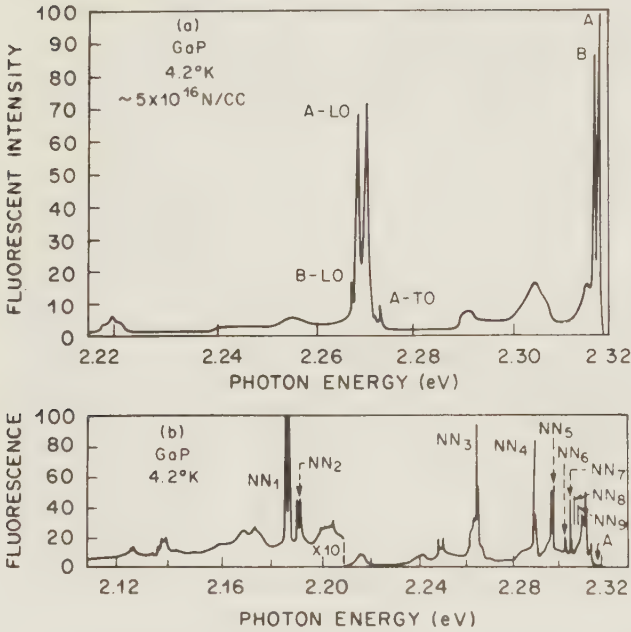


Fig. 8. Excitons bound to isolated N atoms (upper) and NN pairs (lower) [45].

The difference shows that the binding mechanisms of the two centres are quite different. The electronic binding to N is apparently dominated by short range interactions, giving a highly extended wavefunction in the wavevector space. This is in contrast to the effective-mass-like character of donor excitons. As a result of this difference, the magnitude of the electron wavefunction at $k = 0$, where the hole wavefunction has its maximum, is much higher for the N exciton than for donor excitons. This produces a large total oscillator strength for the N exciton, a factor 100 larger than for the exciton bound

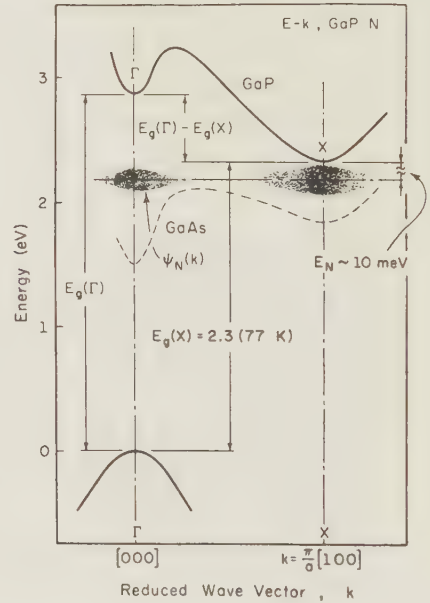


Fig. 9. Electron wavefunction of the nitrogen bound exciton [2].

to S_p in GaP. Experimental results for other isoelectronic impurities in GaP, such as As, Sb and Bi, are similar [2]. The wide spread of the electron wavefunction of a nitrogen bound exciton is illustrated in Fig. 9.

It has been shown that there is a further increase in the N oscillator strength (by about a factor 1000) [2] for $X = 0.45$ in $\text{GaAs}_{1-X}\text{P}_X$. This is near the point where the bandgap becomes direct as in GaAs. The direct bandgap of GaAs is indicated by the broken line in Fig. 9. However, a corresponding decrease in the radiative lifetime is noted. These aspects of isoelectronic traps are very important in applications, particularly for light-emitting diodes. In this way, the disadvantage of indirect bandgaps can be overcome.

A different category of isoelectronic defects is the class of molecular centres. The simplest of these are the axial centres formed from associated pairs of simple donors and acceptors on substitutional sites. Two well-known examples are Zn-O and Cd-O in GaP [34-36]. Here, nearest-neighbour pairs of GaP are replaced by $\text{Zn}_{\text{Ga}}-\text{O}_\text{P}$ or $\text{Cd}_{\text{Ga}}-\text{O}_\text{P}$ forming deep bound states for electrons. The binding mechanism of these centres can be understood in the HTL model, since the hole is weakly bound in the Coulomb field of the electron. These donor-acceptor pairs on nearest neighbour sites are closely related to the case of pair emission (cf. Eq. 2). It has been observed that for several centres of this form involving the deep donor O_P in GaP, the binding energy E_D of the electron is reduced by a Coulombic interaction to $E_D - e^2/\epsilon R$. Here, ϵ is the static dielectric constant and the pair separation is R . A bound state occurs if $(E_A + E_D)$ is significantly greater than $e^2/\epsilon R$, which is typically 0.5 eV for nearest neighbours in GaP [26].

A related centre is the slightly more complex $\text{Li}_\text{I}-\text{Li}_{\text{Ga}}-\text{O}_\text{P}$ centre in GaP [53]. The donor part is O on a P site. The substitution of two Li atoms at one of the neighbouring Ga sites is equivalent to placing a single ionized acceptor on a lattice site adjacent to the O_P donor. In this case too, binding of the exciton is mainly due to the electron binding to the deep O_P donor. Several other excitons believed to be bound to nearest-neighbour pairs have been observed [26]. However, not all have as yet been positively identified.

In this work, more complicated defects are defined as isoelectronic, if they fulfil local bonding requirements and are neutral and spin-free in the ground state. In addition, it is required that there are no incomplete d-shells in the complex [54]. In this case, the bound exciton consists of only two particles, without coupling to additional particles at the centre. Examples of this type of molecular centres are, e.g., $\text{Cu}_\text{I}-\text{Cu}_{\text{Ga}}-\text{Cu}_\text{I}$ and $\text{Li}_\text{I}-\text{Cu}_{\text{Ga}}-\text{Li}_\text{I}$, which are presented in the papers below.

Electronic structure

Excitons bound to isoelectronic centres generally show a simpler electronic structure than is the case for those bound to neutral acceptors and donors. The former consist of merely two particles bound to a neutral centre unlike the latter where a third particle is also present. The simplest case occurs when the impurity site is of high symmetry. In the zincblende lattice, a substitutional impurity site has full tetrahedral symmetry T_d . An exciton is formed when the $J = 0$ centre binds a hole from the uppermost valence band (Γ_8 , $j=3/2$) and an electron from the lowest conduction band (Γ_6 , $j=1/2$). In Fig. 10, some well-known bound excitons illustrate different combinations of local crystal-field splittings and J-J splittings [13]. In Fig. 10a, the extreme case of InP:Bi is shown [55]. Because of the small ratio m_e^*/m_h^* for InP, the electron-hole overlap and hence the J-J splitting is negligible.

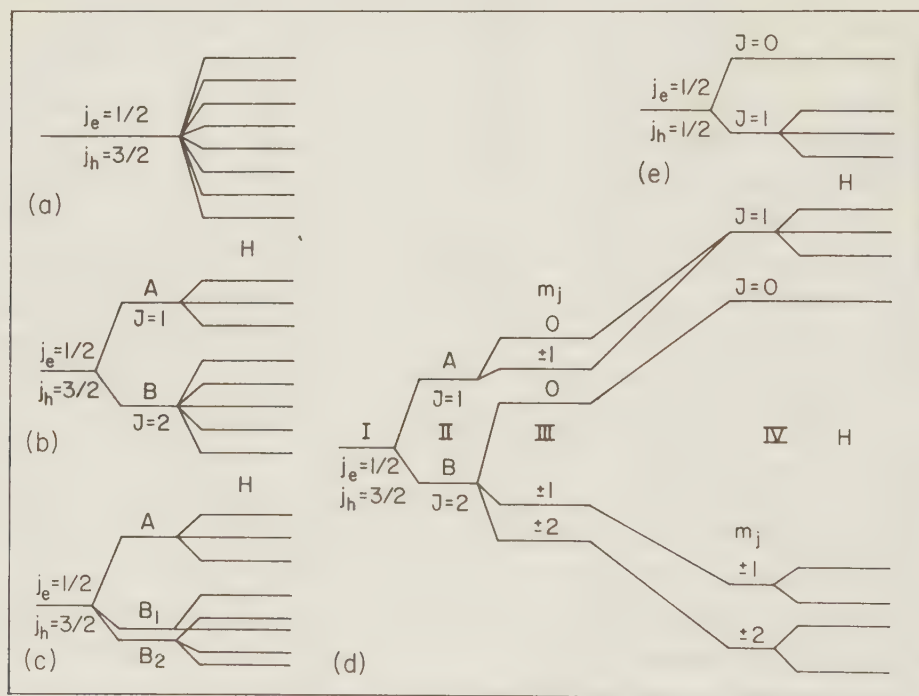


Fig. 10. Effects of crystal field and exchange interaction on BE states.

Usually, the J-J splitting is larger as exemplified by GaP:N shown in Fig. 10b [45]. In this case, the electron and hole couple to give total angular momentum of $J = 1$ and $J = 2$ for the exciton, $J = 2$ being lower in energy. This state is heavily favoured by thermalization at low temperatures. Therefore the forbidden transition to the $J = 0$ ground state is observed (the nitrogen B line). At higher temperatures, transitions from the $J = 1$ state give the allowed A line in luminescence. In a stronger T_d crystal field, the fivefold degeneracy of the $J = 2$ level

is split into a triplet (T_2) and a doublet (E), according to the maximum orbital degeneracy allowed in T_d symmetry. This is shown in Fig. 10c for, e.g., GaP:Bi [56].

Excitons bound at molecular isoelectronic defects inevitably experience a local axial strain field. The field is of different strength and sign (tensional or compressional) according to the relative size of the atoms replacing the host atoms. Also, interstitial atoms introduced into the lattice may cause a compressional strain field. The impurities Cd-0 and Zn-0 in GaP have been found to produce effects equivalent to an internal uniaxial tension, as can be recognized by the splitting of the valence band states [57]. In Fig. 10d, the effect on the BE states of a gradually increasing crystal field corresponding to local uniaxial tension is shown [13]. It is well established that the effect of an axial field on the valence band states is to split the uppermost Γ_8 band into two components $|3/2, \pm 3/2\rangle$ and $|3/2, \pm 1/2\rangle$, where the $|j m_j\rangle$ notation is used [57]. The projection of the momentum of the hole states along the axis (m_j) remains a good quantum number for weak fields. Depending on the sign of the axial field, either of these split states will be split off by the field. A similar splitting occurs for the BE states derived from the hole states. (cf. Fig.4).

Apart from the orientational degeneracy present in the case of the crystal field, the behaviour of the BE states in Fig. 10d, is qualitatively similar to that of an external uniaxial tension of appropriate symmetry. In part ii, the same case as for the N exciton in Fig. 10b is shown. In part iii, the local crystal field is of moderate strength, small compared with the spin-orbit splitting of the valence band but large compared with the J-J coupling. Here, components of the angular momentum $\pm m_j$ along the crystal field axis remain degenerate. Transitions from the $|J, m_j\rangle$ states with $J=2$ are forbidden, but mixing of the states $|2, \pm 1\rangle$ and $|1, \pm 1\rangle$ makes transitions from the former allowed. For $\text{Li}_I\text{-Li}_{\text{Ga}}\text{-O}_P$ the total splitting is 4.6 meV, and four out of the five substates have been recognized at slightly different temperatures [53]. In a stronger tensional axial field as is the case for Zn-0 and Cd-0, only the lowest two states have been recognized [34,35,36].

In the limit of a very strong axial field, the crystal field splitting exceeds the spin-orbit splitting and the situation shown in part IV may occur. The spin and angular orbital momenta are decoupled in the presence of a strong crystal field. The spin is not coupled directly to the field and remains unaffected. However, the orbital angular momentum of one of the three p states (the one transforming as p_z) is quenched. This leaves a pure spin state for the hole with $s=1/2$ and the BE states are then formed by the coupling of two pure spin particles. As shown uppermost in part IV of Fig. 10d, the states $J=0$ and $J=1$ for the bound excitons result. For the opposite sign of the

local strain field (a compressional field), the singlet-triplet states are lowest in energy of all the BE states as shown in Fig. 10e. Because of the large splitting, only the lower group of states can be seen in emission. The upper group (Fig. 10d) is only seen in optical absorption, if the lines are not too much lifetime broadened.

A singlet-triplet pair is observed for the S_p - Ge_p bound exciton in GaP [14]. This is also observed for the COL and the 1.911 eV bound excitons in GaP, which are thoroughly discussed in this work. The systems showing the triplet-singlet BE structure described here, have not been extensively studied until now. It is of considerable importance to understand the details of the behaviour outlined above. This includes the local strain field and strong exchange interaction causing the observed BE spectra. A better knowledge of this systems is a clue to the explanation of many hitherto unexplained phenomena in defect spectroscopy.

Vibronic transitions in optical spectra

As already mentioned, momentum-conserving phonons greatly enhance the oscillator strength for transitions involving weakly bound impurities in semiconductors with indirect bandgap. In this case the delocalization of the wavefunctions emphasizes different aspects of the coupling to phonons as compared with more localized systems.

If a system is composed of a lattice and a point defect with two orbitally non-degenerate states, a ground state and an excited state, the Hamiltonian for the total system of nuclei and electrons is

$$H = T_e + T_n + V_e + V_n + V_{en}, \quad (3)$$

with T the kinetic energy and V the potential energy. The subscript e refers to electronic coordinates r and n to nuclear coordinates q . In the adiabatic and the zeroth order Born-Oppenheimer approximations [58] the vibronic wavefunction of the total system can be written

$$\Psi(r, q) = \psi(r, q) \chi(q) \quad (4)$$

The electronic wavefunction ψ is a solution of

$$(T_e + V_e + V_n + V_{en}) \psi(r, q) = \epsilon_e(q) \psi(r, q). \quad (5)$$

By omitting T_n , the nuclei are assumed to be infinitely heavy. In practice the electronic states $\psi(r)$ are often used instead of $\psi(r, q)$. The nuclear vibrational state χ is obtained from the equation

$$(T_n + \epsilon_e(q)) \chi(q) = E\chi(q) \quad (6)$$

As a consequence of the adiabatic approximation, the slow nuclei are described as moving in the effective potential $\epsilon_e(q)$ of rapidly moving electrons and this motion depends on the electronic state. Expansion of $\epsilon_e(q)$ about equilibrium commonly leads to a quadratic function of q , in which case Eq. 6 resembles the equation of a set of harmonic oscillators.

The configuration coordinate model is often used to treat the electron-vibrational coupling, especially in the strong-coupling limit. The defect and a small number of its nearest neighbours are then considered. An extreme case is that of strong coupling to a single lattice coordinate, which may be a normal-mode coordinate of the crystal or a configuration coordinate, representing the displacements of neighbouring ions. In the simplest version of this model [33], the two non-degenerate electronic states ψ_a and ψ_b at the defect are assumed to couple linearly to a normal coordinate q of the lattice. To solve the nuclear problem, the appropriate potentials for the two electronic states are given by (see Fig. 11 a)

$$\epsilon_a = 1/2 M\omega^2 q^2 \quad (7a)$$

$$\epsilon_b = 1/2 M\omega^2 q^2 + E_{ab} - A \hbar\omega(M\omega/\hbar)^{1/2} q \quad (7b)$$

The dimensionless constant A is a measure of the linear coupling which displaces the equilibrium position of the mode, without changing its frequency ω . M is the effective mass for the mode and E_{ab} denotes the energy separation of the two states at $q = 0$. The solutions $\chi_{am}(q)$ and $\chi_{bn}(q)$ of Eq. 6 are harmonic oscillator wavefunctions with energy eigenvalues

$$E_{am} = (m + 1/2)\hbar\omega \quad (8a)$$

$$E_{bn} = (n + 1/2)\hbar\omega + E_{ab} - 1/2 A^2 \hbar\omega \quad (8b)$$

for the ground state and the excited state respectively.

The vibronic functions for the coupled defect are the product functions $\psi_a(r,q) \chi_{am}(q)$ and $\psi_b(r,q) \chi_{bn}(q)$. The probability for an optical transition between these states is proportional to the squared dipole matrix element $\langle \psi_b \chi_{bn} | \vec{r} | \psi_a \chi_{am} \rangle$. In the Condon approximation, the electric dipole moment is assumed to be independent of q , so that the matrix element can be separated in the form $\langle \psi_b | \vec{r} | \psi_a \rangle \langle \chi_{bn} | \chi_{am} \rangle$.

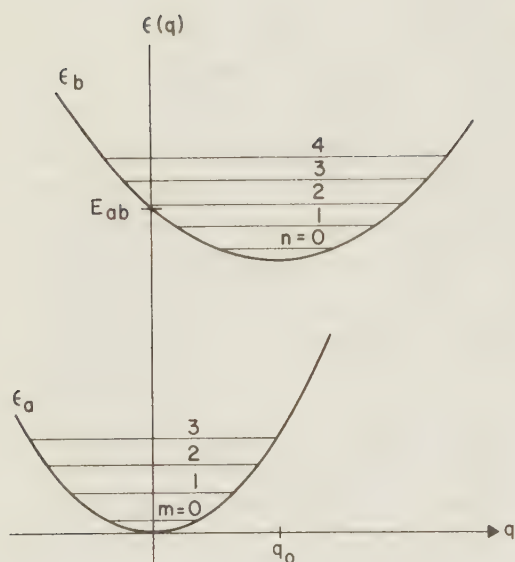


Fig. 11a. Configuration coordinate diagram for two electronic states ϵ_a and ϵ_b . Vibrational levels for each state are indicated.

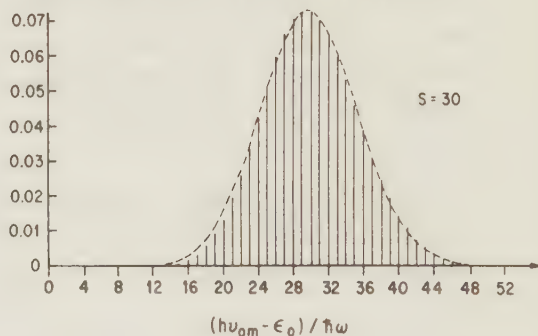
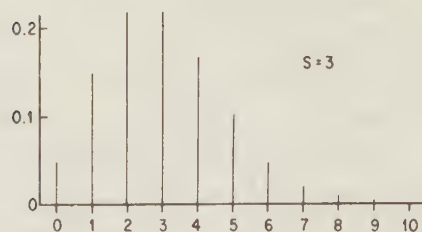
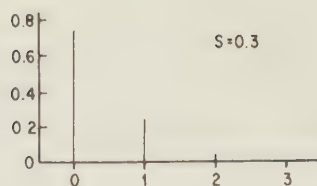


Fig. 11b. Normalized probabilities for transitions between the $m=0$ and the n levels in a). Three different coupling strengths are illustrated. For $S=30$ a Gaussian envelope is included.



Fig. 12. Hypothetical emission spectrum for coupling to a discrete phonon mode. Also a smooth band from coupling to other modes is present.

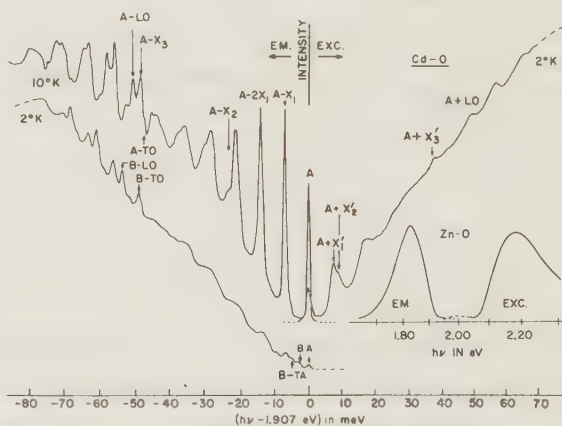


Fig. 13. Examples of strong coupling in bound exciton spectra: Cd-O and Zn-O (in the inset).

Thus, the optical line-shape is determined by the vibrational overlap integral [59]. Introducing the Huang-Rhys factor $S = A^2/2$ as an alternative measure of the coupling strength, the normalized transition probability is

$$|\langle \chi_{bn} | \chi_{am} \rangle|^2 = e^{-S} \left(\frac{m!}{n!} \right) S^{n-m} \left(L_m^{n-m}(S) \right)^2 \quad (9)$$

where $L_p^q(x)$ is the associated Laguerre polynomial. At $T = 0$ K, the only occupied level is $m = 0$, and consequently the transition probability to the n -th level of the excited state is

$$|\langle \chi_{bn} | \chi_{a0} \rangle|^2 = e^{-S} \frac{S^n}{n!} \quad (10)$$

i.e., the simple Poisson function.

This gives an absorption spectrum consisting of a number of equally spaced lines at frequencies $E_n = (E_{ab} - S\hbar\omega) + n\hbar\omega = E_0 + n\hbar\omega$, as illustrated in Fig. 11b for three different values of S . The zero-phonon line at E_0 has the normalized probability e^{-S} and the peak intensity of the phonon sideband occurs at $n \approx S$. For strong coupling, the envelope of the spectrum approaches a Gaussian band shape as shown in the figure for $S = 30$. If emission occurs between the same pair of discrete states, a series of lines is expected at energies $E_m = E_0 - m\hbar\omega$ mirrored about the zero phonon line.

In Fig. 12 an example of an emission band characteristic for a strong coupling to a single mode is shown. Also, coupling to other modes gives a smooth emission sideband, on which the discrete replicas are superimposed. This type of spectra is very common. The case of the Cd-0 BE in GaP is shown in Fig 13. This spectrum is characteristic for strong coupling to local modes. An interesting feature is that the local modes appear only in the A spectrum, dominating at 10 K [35]. In the inset the Zn-0 BE spectrum is shown. The very strong phonon coupling can be estimated from the energy difference between the emission and absorption maxima.

The procedure can be generalized to arbitrary temperatures by introducing the thermal occupation probabilities in the initial state through Boltzmann factors. The crude model summarized above can be extended to include quadratic electron-phonon coupling [59]. Also, a generalization to more than one mode is straight forward [60]. The case of degenerate electronic states is more complicated. The Jahn-Teller theorem states that an electronic state in a symmetrical environment will distort to a configuration of lower symmetry, if degenerate. This induces complex vibronic coupling [30].

Summary of the papers

The first two papers contain studies of GaN grown by vapour-phase epitaxy on sapphire.

In paper I below, photoluminescence studies of Zn-doped GaN are reported. Undoped GaN single crystals are always found to be of low ohmic n-type and therefore acceptor dopants are of particular interest. The bandgap of GaN is 3.5 eV at 0 K, sufficiently large for emissions in the blue region. Zn-doping gives four different emissions, all of them broadened by rather strong phonon coupling. The A emission at highest energy (peaking at 2.87 eV) shows clear phonon replicas with a phonon energy of 74 meV, which is in the optical phonon branch of GaN. The spectral shape of this emission has been analysed using the simple model of linear coupling outlined above. Such evaluation is of importance when estimating the strength of the overlap between the different emissions. A similar analysis for the C emission (peaking at 2.2 eV) is made. This shows a phonon structure with phonon energy 83 meV.

In paper II, the optical cross-sections of the acceptor levels corresponding to the four emissions in Zn-doped GaN are measured using the photoluminescence excitation method. By comparing the overlap between the normalized transition probabilities for emission and absorption, respectively, an estimate of the size of the electronic broadening is obtained. This provides values for two of the acceptor levels, $E_A = 0.34$ eV and $E_C = 1.02$ eV. The binding energies of E_B and E_D are also estimated. The cross-sections for the A and C levels are analysed at different temperatures, assuming the linear coupling mechanism with phonon energies obtained from the emission spectra. The thermal broadening of the absorption cross sections is compared with theoretical expectations from the linear coupling model.

In papers III-VI, an investigation of the optical properties of Cu-doped GaP is presented.

Paper III contains a study of the COL centre in GaP, which is shown to involve three Cu atoms. The photoluminescence spectra for this emission are combined with PLE data, measured with excitations from a tunable dye-laser. The emission spectrum shows a complicated phonon structure. This is consistent with a model of two interstitial Cu_I atoms and a substitutional Cu_{Ga} atom as the identity of the neutral isoelectronic COL centre. From the very complex structure of the PLE spectrum and magneto-optical measurements, it is concluded that both particles of the exciton are considerable localized giving greater overlap than is usual for bound excitons. Also, the BE is subject to a strong local axial field which is shown to explain the singlet-triplet-nature of the BE states.

In paper IV, the investigations of the COL centre are continued with

measurements of the emission at temperatures up to room temperature. The thermal activation energy for the total emission intensity is evaluated and found to be close to the exciton localization energy. This suggests that the bound exciton is thermally released as a whole entity. In the paper, a theoretical expression is fitted to the temperature dependence of the integrated intensity of the electronic line. The model employed involves both coupling to several discrete phonon modes with coupling strengths evaluated from the emission spectrum and coupling to the continuous acoustic bands of GaP. The variation of the integrated intensity of the electronic line and the relative contributions of different terms are explained according to this model. Also, the vibrational properties of the COL emission observed are discussed in relation to the defect identity suggested in paper III.

In paper V, the effect of Li-doping on the Cu-doped crystals studied in papers II and IV is investigated. It is found that the COL emission and the 1.911 eV emission (paper VI) disappear in favour of four new emissions. These emissions are related to Cu and Li doping and are reported here for the first time. Both photoluminescence data and PLE data are presented for the centres in the cases where PLE spectra were obtainable. Also, magneto-optical Zeeman work is reported. Models for the identity of the four Cu-Li centres are given, based on evidence from doping, localization energy, phonon coupling and general experience from the earlier work on Cu-doping.

Finally, paper VI presents a detailed study of the Cu centre giving the BE emission at 1.911 eV. This emission is present as the result of Cu doping at high diffusion temperatures. The phonon coupling of this emission is discussed and studied at different temperatures and the thermal activation energy deduced. PLE measurements reveal a strong absorption edge with rich structure showing similar phonon coupling, but displaced 90 meV above the BE ground state. This is shown to be the result of a strong crystal field splitting of the bound hole states of the BE, explaining the isotopic behaviour of the ground state triplet of the BE found in magneto-optical measurements. ODMR data firmly establish the orientation of the defect binding the excitons as $\langle 100 \rangle$ and a model of the defect consistent with this symmetry axis is given. Its relation to other Cu centres is also discussed.

Acknowledgements

I am deeply indebted to Dr. Bo Monemar for introducing me into this field. The work has been made possible through his stimulating cooperation and encouragement over the years.

Also, I wish to express my sincere thanks to Professor Hermann G. Grimmeiss for his support and interest in my work.

I am grateful to my co-authors for their collaboration and many fruitful discussions. I owe special thanks to Dr. Olle Lagerstedt for a stimulating collaboration.

My thanks to Eva Dagnegård and Birgitta Warhed who have typed the manuscript. Also, I am grateful to Sven Andersson for his excellent graphical work.

Finally, I want to thank all my friends at the Department of Solid State Physics for valuable discussions and their companionship during this work.

References

1. See e.g. R.K. Willardson and A.C. Beer, ed., Semiconductors and Semi-metals, Vol. I-IV (Academic Press, 1966-1968)
2. P.J. Dean in Topics in Applied Physics, Vol. 17, Electroluminescence, ed. J.I. Pankove (Springer Verlag, Berlin, 1977)
3. A.A. Bergh and P.J. Dean, Light Emitting Diodes (Clarendon, Oxford, 1976)
4. B. Monemar, Phys. Rev. B 10, 676 (1974)
5. O. Lagerstedt and B. Monemar, J. Appl. Phys. 45, 2262 (1974)
6. J.I. Pankove and J.E. Berkeyheiser, J. Appl. Phys. 45, 3892 (1974)
7. J.I. Pankove, E.A. Miller and J.E. Berkeyheiser, J. Luminescence 5, 84 (1972)
8. O. Lagerstedt, B. Monemar and H.P. Gislason, J. Appl. Phys. 49, 2953 (1978)
9. This blue-emitting diode will be made by Matsushita, Japan.
10. J.I. Pankove, ed., Topics in Applied Physics, Vol. 17, Electroluminescence (Springer Verlag, Berlin, 1977)
11. M.L. Cohen and T.K. Bergstresser, Phys. Rev. 141, 789 (1966)
12. T.N. Morgan, Phys. Rev. Lett. 21, 819 (1968)
13. P.J. Dean and D.C. Herbert in Topics in Current Physics, Vol. 14, Excitons, ed. K. Cho (Springer Verlag, 1979) pp 55-182
14. P.J. Dean, W. Schairer, M. Lorentz and T.N. Morgan, J. Luminescence 9, 343 (1974)
15. R. Madar, D. Michel, G. Jacob and M. Boulou, J. Crystal Growth 40, 239 (1977)
16. O. Lagerstedt and B. Monemar, Phys. Rev. B 19, 3064 (1979)
17. S. Bloom, G. Harbeke, E. Meier and I.B. Ortenburger, phys. stat. sol. (b) 66, 161 (1974)
18. J.I. Pankove, S. Bloom and G. Harbeke, RCA Review 36, 163 (1975)
19. D.D. Manchon, A.S. Barker, P.J. Dean and R.B. Zetterstrom, Solid State Commun. 8, 1227 (1970)
20. W. Shockley, Electrons and Holes in Semiconductors (Van Nostrand, New York, 1950)
21. S.T. Pantelides, Rev. Mod. Phys. 50, 797 (1978)
22. M. Jaros, Advances in Physics, 29, 409 (1980)
23. W. Kohn in Solid State Physics, ed. F. Seitz and D. Turnbull (Academic Press, New York, 1957) Vol. 5
24. H.G. Grimmeiss, Ann. Rev. Mater. Sci. 7, 341 (1977)
25. G.J. Rees, H.G. Grimmeiss, E. Janzén and B. Skarstam, J. Phys. C 13 6157 (1980)

26. P.J. Dean, J. Luminescence 7, 51 (1973)
27. J.J. Hopfield, D.G. Thomas and M. Gershenzon, Phys. Rev. Lett. 10, 162 (1963)
28. P.J. Dean, Progress in Solid State Chemistry 8, 1 (New York, 1973)
29. F.E. Williams, phys. stat. sol. 25, 493 (1968)
30. R.K. Watts in Point Defects in Crystals (John Wiley, 1977)
31. P.J. Dean and L. Patrick, Phys. Rev. B 2, 1888 (1970)
32. R.A. Street and W. Senske, Phys. Rev. Lett. 37, 1292 (1976)
33. B. Monemar and L. Samuelson, J. Luminescence 12/13, 507 (1976); Phys. Rev. B 18, 809 (1978)
34. C.H. Henry, P.J. Dean and J.D. Cuthbert, Phys. Rev. 166, 754 (1968)
35. T.N. Morgan, B. Welber and R.N. Bhargava, Phys. Rev. 166, 751 (1968)
36. J.M. Dishman and M. DiDomenico, Phys. Rev. B 4, 2621 (1971)
37. P.J. Dean, D.J. Robbins, S.G. Bishop, J.A. Savage and P. Porteous, J. Phys. C 14, 2847 (1981)
38. F. Vollot, J. Barrau, M. Brousseau and J.C. Brabant, J. Phys. C 14, 1855 (1981)
39. D.J. Robbins, Proceedings of the ICL, Berlin, 1981, J. Luminescence
40. J. Frenkel, Phys. Rev. 37, 1276 (1931)
41. G.M. Wannier, Phys. Rev. 52, 191 (1937)
42. N.F. Mott, Proc. R. Soc. A 167, 384 (1938)
43. M. Lampert, Phys. Rev. Lett. 1, 450 (1958)
44. J.R. Haynes, Phys. Rev. Lett. 4, 361 (1960)
45. D.G. Thomas, J.J. Hopfield and C.J. Frosch, Phys. Rev. Lett. 15 857 (1965);
D.G. Thomas and J.J. Hopfield, Phys. Rev. 150, 680 (1966)
46. P.J. Dean, J.D. Cuthbert, D.G. Thomas and R.T. Lynch, Phys. Rev. Lett. 18, 122 (1967)
47. P.J. Dean, D.D. Manchon, Jr and J.J. Hopfield, Phys. Rev. Lett. 25, 1270 (1970)
48. J.L. Mertz, R.A. Faulkner and P.J. Dean, Phys. Rev. 188, 1228 (1969)
49. J.J. Hopfield, Proc. Int. Conf. Physics of Semiconductors, Paris 1964 (Dunod, Paris, 1964) p 725
50. J.W. Allen, P.J. Dean and A.M. White, J. Phys. C 9, L113 (1976)
51. J.J. Hopfield, D.G. Thomas and R.T. Lynch, Phys. Rev. Lett. 17, 312 (1966)
52. E. Cohen and M.D. Sturge, Phys. Rev. B 15, 1039 (1977)
53. P.J. Dean, Phys. Rev. B 4, 2596 (1971)
54. Other definitions exist, see, e.g., D.J. Robbins and P.J. Dean, Advances in Physics, 27, 499 (1978) and Ref. 21

55. A.M. White, P.J. Dean, K.M. Fairhurst, W. Bardsley and B. Day,
J. Phys. C 7, L35 (1974)
56. P.J. Dean and R.A. Faulkner, Phys. Rev. 185, 1064 (1969)
57. J. van W. Morgan and T.N. Morgan, Phys. Rev. B 1, 739 (1970)
58. M. Born and R. Oppenheimer, Ann. Phys. 84, 457 (1927)
59. T. Keil, Phys. Rev. 140, A 601 (1965)
60. K.K. Rebane, Impurity Spectra of Solids (Plenum Press, New York, 1970)

Optical properties of the Cu-related COL centre in GaP

B. Monemar and H.P. Gislason

University of Lund, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

P.J. Dean and D.C. Herbert

RSRE, Gt Malvern, Worcs WR14 3PS, England

Abstract

A detailed investigation on optical properties of the COL-centre in GaP is reported, combining photoluminescence data with dye laser excited excitation spectra. Evidence from the doping conditions required to produce this defect suggests an identification of the COL-centre with a defect containing Cu only. The novel optical data support this view, since the COL spectrum is identified as originating from an exciton bound to a non-linear isoelectronic $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ associate. The complicated local mode coupling and the rather strong coupling to the lattice continuum modes is expected for such a defect structure, where the Cu_{Ga} can be considerably relaxed. The strong compressive axial strain field created by this defect causes a splitting of the hole states at the defect and decouples the spin and orbital angular momentum of these states. For a complete decoupling the bound exciton is formed by combining a pure spin hole state and an electron. This results in the observed $J=1$ spin triplet as the lowest bound exciton state and a higher $J=0$ singlet state. From the rich structure observed in excitation spectra a large exchange splitting of 23.2 meV is obtained between the $J=1$ ground state and the $J=0$ state. No orbitally excited states of one particle in the Coulomb field of the other are

observed for this bound exciton, probably a consequence of the fact that both electronic particles are relatively deeply bound. A typical feature for this class of defects seems to be that transitions involving the singlet $J=0$ state have a much stronger total oscillator strength than those involving the $J=1$ ground state. This is a consequence of a spin selection rule $\Delta S=0$, also manifested by the long decay time of the $J=1$ bound exciton emission ($\tau \approx 100 \mu\text{s}$).

1. Introduction

Cu is known to be easily incorporated into GaP as a contaminant during growth or heat treatment. Several investigations on bound electronic states associated with Cu in GaP have been published during the last two decades [1-12], and a large number of different Cu-related defects seems to be present in material prepared by different methods. The origin of these Cu-related defect levels has not been identified in any case from the data presently available [1-12], although vague indications for the presence of complex centres have been presented in some cases [5, 6, 10, 11]. This problem of defect identification is of course not restricted to Cu in GaP, but rather is common to most deep level defects in semiconductors. Obviously, for the case of Cu in GaP, considerably more detailed experimental data are necessary to assist in such defect identification.

The electronic behaviour of Cu in GaP is not easily predictable at this stage. A simple substitutional Cu_{Ga} acceptor state may not exist, at least not on an undistorted lattice site. Recent EPR-data do not reveal any sign of such an undistorted Cu_{Ga} state [13]. On the other hand, Raman scattering data for Cu acceptors in GaP have recently been interpreted as an indication of the prominence of just such a simple substitutional

acceptor state [14].

Several of the Cu-related centres in GaP are found to give radiative recombination, which allows detailed information to be obtained from photoluminescence (PL) measurements. In particular, bound exciton spectra which give sharp electronic lines in emission and absorption, have proved to be very useful in characterizing defect centres in III-V and II-VI compounds [15]. If one looks at the situation in other III-V compounds, such as GaAs, bound exciton spectra believed to be related to Cu-acceptors with binding energies 0.15 eV and 0.47 eV respectively, have indeed been found, and the Cu-related defects involved were found to have a symmetry lower than cubic in both cases [16]. Sharp line structure has actually been observed previously for some deep Cu-related centres in GaP [5, 6, 11], and tentatively interpreted as due to bound exciton recombinations.

In the present investigation we focus our attention to the prominent 2.1774 eV COL (characteristic orange luminescence) emission in Cu-diffused GaP. As already mentioned, preliminary PL investigations on this emission were published several years ago [17-19]. Unfortunately the early literature was misleading in one important aspect, ascribing the spectrum to a $V_{Ga}-O_P$ complex [17-19]. This was later shown to be in error, and the emission was linked to Cu via isotope shift analysis in PL data [5,6]. At that time only emission spectra could be observed, since with conventional light sources, the absorption for this COL transition was too weak to be detected due to a low oscillator strength [17]. With the availability of cw dye lasers this problem can now be overcome. In this paper is included complementary absorption data, taken as excitation spectra (PLE) of the low temperature COL emission. A rich structure of higher electronic states is found in these low temperature PLE data, unrevealed in PL data. The interpretation of these spectra is simplified by studies of Zeeman splitting in magnetic field up to 3.5 T.

In Sec. II below, information is given on the preparation of the Cu-doped samples used in this investigation, together with details of the experimental procedure. Experimental data for PL spectra of this COL emission are discussed briefly in Sec. III, and serve as a comparison with absorption data. Section IV contains the absorption data from PLE-measurements, which show a rich structure due to excited electronic states and a complicated phonon coupling to the bound exciton (BE) transitions. In Sec. V, the detailed observations from both emission and absorption spectra are discussed in relation to a suggested model of a $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ defect, to which the exciton is bound.

II. Samples and experimental procedure

Several different types of GaP samples were used in these investigations, Cu-doped as well as undoped for reference. Most experiments were carried out on nominally undoped layers grown by liquid phase epitaxy (LPE), which were Cu-diffused in the temperature range 900–1100 °C. Such crystals showed rather strong COL luminescence, with minimal interference with other emissions, since the shallow DA-pair spectra peaking at about 2.2 eV were of very low intensity. To be able to exclude possible effects from the substrate material, experiments were also carried out on bulk crystals. Some of those were liquid encapsulated Czochralski (LEC) grown material, others were needles grown by the wet H_2 transport technique, Cu-contaminated accidentally during growth. These samples showed similar results for the COL emission, but the needles suffered from a much reduced PL intensity. Other bulk samples were solution grown in a temperature cycle 1000 °C → 800 °C, with Cu and sometimes Te (to produce n-type material) in the solution. It has not been possible to correlate the occurrence of the

COL spectrum with any shallow donor dopants (in addition to Cu), in agreement with earlier studies [5]. On the other hand it was established that the COL emission can easily be produced by Cu-diffusion at 900 - 1100 °C in both n-type and p-type GaP.

Steady state photoluminescence (PL) spectra were obtained, either with Ar^+ or Kr^+ laser excitation, or with selective excitation from cw dye lasers, employing suitable dye solutions. For excitation spectra (PLE) the dye laser wavelength was continuously scanned with a controlled drive unit. To further reduce the straylight level from the dye laser, in the case of weak emission intensity, it was combined with a synchronously scanned grating filter. The spectral linewidth of the dye laser was about 0.3 Å, and a similar linewidth could be maintained on the detection side. There we used a Jarrel Ash 0.75 m double grating monochromator for the recording of PL spectra, and for the selection of a suitable wavelength in recording PLE spectra. For studies of PL and PLE spectra in a magnetic field, a 3.5 T Varian electromagnet was employed together with a 2 m Bausch and Lomb spectrograph equipped with a scanning exit slit and photomultiplier detector. The 2.1774 eV photoluminescence band is sufficiently broad that PLE spectra were readily obtained from the most strongly luminescent sample using a low energy pass filter to reduce the intensity of scattered light in the single monochromator, even when the PLE spectrum was recorded from the region of the 2.1774 eV no-phonon line.

III. Photoluminescence spectra

PL spectra were recorded for a large number of Cu-doped GaP samples between 1.8 K and 140 K. A typical low temperature spectrum of a Cu-diffused sample with a fairly strong orange COL emission is shown in Fig. 1.

From measurements on different types of samples it seems that this emission is strong in all samples diffused with Cu at high temperatures (900 - 1100 °C) and rapidly quenched, as was previously reported [5,18]. As already mentioned, the COL emission is most easily studied in samples with a low shallow level doping, since in this case the background from shallow donor-acceptor pair emissions is much reduced.

The spectrum shown in Fig. 1 is similar to the one earlier published [5, 6, 17, 19], and consists of a zero-phonon line at 2.1774 eV at 1.8 K (which in high resolution actually shows a ~ 0.15 meV splitting [6]), together with a dominating and complicated phonon-assisted wing extending down to about 1.9 eV. The zero-phonon line appears very sharp at the lowest temperatures (usually the linewidth was resolution limited to 0.15 meV at 1.8 K). The zero-phonon line is followed on the low energy side by a broad continuum background, due to coupling with low energy phonons in the acoustic band. Starting at 5.3 meV below the zero-phonon line, a discrete phonon spectrum is superimposed on the continuum background, with several discrete quasilocalized phonon modes, as listed in Table 1. The total emission envelope has a considerable width, and the dominating background must be regarded as a convolution of a continuum one-phonon spectrum, displacing the peak of the envelope some 65 meV below the zero-phonon line in emission (Fig. 1).

In the temperature range 5-20 K we observe anti-Stokes replicas for the discrete phonon replicas L_1 - L_3 (Table 1) as also shown in detail in Fig. 1. These observations directly confirm that the features L_1 - L_3 are phonon replicas, and not electronic transitions. Apparently these discrete phonons are of somewhat smaller energy in the upper electronic state of the optical transition (Table 1). This is in agreement with the data from PLE spectra to be presented below. The temperature dependence of the

discrete line spectrum and the total envelope of the COL-emission has been investigated in detail, and will be included in a separate publication [20].

IV. Excitation spectra

The optical transition responsible for the COL emission has a low oscillator strength, which means that excitation spectra cannot be obtained in the conventional way [17]. A tuneable dye laser provides both adequate intensity and spectral resolution for detection of narrow absorption lines. The intensities of both the no-phonon line and the total emission are linear functions of the excitation intensity for this emission. Therefore, the excitation spectrum is directly proportional to the absorption coefficient, after a linear correction for the variation of excitation intensity.

A typical PLE spectrum for the COL emission at 2 K is shown in Fig. 2. An experimental difficulty in the measurements was the presence of a strong continuum background in the PLE spectrum. This background appears to be caused by excitation of the COL centre through capture of photoexcited free carriers, which are in turn produced by two-step excitations via deep levels within the bandgap. Such two-step excitations have been shown to be rather efficient for common deep levels such as 0 in GaP [21-22]. The general impression from the spectrum in Fig. 2 is the presence of strong narrow spectral features from the lowest bound exciton line at 2.1774 eV up to the bandgap energy. Clearly, most of this structure cannot be related to the lowest BE state. Rather it is a manifestation of excited state configurations for the bound exciton under study. This behaviour is remarkable, since usually excited BE states in previously studied absorption spectra for GaP are due to exchange and crystal field splitting at the

order of a few meV from the lowest BE state [15, 23-26], or to a simple hydrogenic series for the excitation of the loosely bound particle in the iso-electronic case [15, 27].

The possibility that these sharp features could be related to other centres than the COL centre has been thoroughly investigated. The PLE spectrum of Fig. 2 was only observed when the detection wavelength was chosen within the range of the COL emission spectrum. In addition it was found that if the dye laser excitation was set to anyone of the sharp lines (Fig. 2), only the usual COL emission was recorded, i.e. no emission specific for some other centre was superimposed. Another important observation is that the sharp lines in excitation disappear with approximately the same thermal quenching behaviour as in the emission [20]. Further, we do not see any coincidence in photon energy between any of the lines and other known centres in GaP, except the well known cases S and N indicated in Fig. 2. The possibility of the observed lines being due to an excitation transfer from such centres can therefore be excluded. This is also supported by the observation that for crystals prepared by quite different techniques (solution growth, LEC growth and wet H₂ transport respectively) these features in Fig. 2 occur with the same relative strength. This observation also excludes the possibility of interference with centres in the substrate material for the LPE layers.

The COL PLE-spectrum starts with the electronic line B₀ at 2.1774 eV (Fig. 2), and up to ~2.20 eV it looks very much like a mirror image of the PL spectrum at the same temperature (Fig. 1). A detailed comparison of the strength of the continuum part of the phonon envelope is difficult, however, due to the presence of a strong background in the PLE data. As shown in more detail in Fig. 3, the three discrete phonon modes L₁, L₂ and L₃ seen in emission are observed in absorption as B₁, B₂ and B₃, but displaced towards lower phonon energies by about 10-15 % (Table 1). These

observations compare favourably with our findings in the anti-Stokes wing of PL-spectra, as reported above, and again confirm that the peaks $L_1 - L_3$ in Fig. 1 are indeed phonon replicas of quasilocalized modes. This conclusion is additionally supported by the magneto-optical data presented below. The relative strengths of these low energy absorption lines $B_1 - B_3$ appear to be significantly different from what is observed in emission (for $L_1 - L_3$) at the same temperature (Fig. 1 and Fig. 3). The line B_1 seems to be only about half as strong as B_2 at 2 K, while L_1 and L_2 are of comparable strength in emission at 2 K. The ratio in absorption corresponds to what is observed in emission at somewhat elevated temperatures [20].

Starting with a sharp line A_0 displaced 23.2 meV above the lowest bound exciton line B_0 , new features are superimposed on the broad phonon assisted wing expected from a mirror image of the ground state emission alone. The energies of these features are tabulated in Table 1. The sharp line A_0 , 23.2 meV above the 2.1774 eV line, does not correspond to the 27.1 meV L_8 phonon mode in emission (Fig. 1), as obvious from the magneto-optical data presented below. We therefore conclude that this A_0 line is of electronic origin. Also, the broad feature A_8 , about 26 meV above B_0 in Fig. 3, has approximately the proper strength and width expected for the L_8 mode in the excited vibronic state of the centre. In that case it is more correctly labelled B_8 .

A much stronger COL-related absorption starts with a group of lines displaced about 30 meV from B_0 , and from there on we believe that phonon replicas related to the B_0 ground state will not be seen. Rather the state A_0 appears to possess a remarkably strong phonon coupling compared with the BE ground state B_0 . The simplest interpretation of the group of three lines $A_1 - A_3$ is that they are phonon replicas of A_0 , and thus generically correspond to the weaker replicas $B_1 - B_3$ of the BE ground state B_0 . This

view is in agreement with magneto-optical data (see below). In analogy with $B_1 - B_3$, A_1 is the lowest line and also the narrowest one, A_2 is the strongest transition, as is B_2 in absorption, while A_3 like B_3 is broad. The phonon energies of the two series do not agree exactly, indicating a stronger non-linearity of phonon coupling connected with the A_0 state, consistent with the increased strength of phonon coupling. A_1 lies 28.2 meV above B_0 , i.e. 5.0 meV above A_0 , while A_2 (29.4 meV above B_0) involves a phonon energy of 6.2 meV and A_3 (31 meV above B_0) a phonon energy about 7.8 meV. These phonon energies are to be compared with the corresponding values for $B_1 - B_3$ in Table 1. Second order replicas with phonon energies corresponding to $A_1 - A_3$ are expected to build up the broad background around A_5 , while the rather sharp peak A_5 might also contain a contribution from a zone boundary TA(X)-replica of A_0 . Similarly the rather sharp line A_6 must contain an additional discrete contribution such as a TA(X)-replica of A_2 . The broad peaks A_7 and A_8 may be replicas of A_0 and A_2 respectively, involving the absorption version of the very strong L_8 mode in emission (Fig. 1). This mode would have an energy of about 26 meV, compare B_8 , which is 26 meV above B_0 .

Line A_9 , 40.7 meV above A_0 , is very sharp, actually only about 30 % broader than A_0 , which in principle makes it a good candidate for electronic transition. Such an interpretation is not readily consistent with the magneto-optical data, however (see below). A sharp local "gap mode" replica of A_0 is the only obvious alternative. A sharp mode L_{12} connected with the BE ground state is observed at similar energy, 39.7 meV in emission (Fig. 1 and Table 1). Such gap modes are often observed to be quite sharp [26]. Similarly the broader peaks $A_{10} - A_{12}$ could correspond to phonon replicas of A_0 in the optical phonon region between 45 and 50 meV. The most plausible assignments of all lines in Figs. 2 and 3 are summarized in Table 1.

In the region above 2.25 eV only weak structure occurs until a very strong and broad line C_0 appears at 2.2864 eV, i.e. 109 meV above the ground state B_0 . Two quite strong and broad replicas of this line occur, C_2 and C_5 , possibly corresponding to the A_2 and A_5 replicas of the A_0 transition. C_0 obviously must be a new electronic transition, and its relation to the other COL-related electronic states is further discussed below. Of the other lines at higher energies only the one at 2.311 eV can not be identified with previously observed bound exciton states related centres other than Cu (such as S and N). This line could therefore correspond to an independent Cu-related centre, possibly the Cu_I donor, binding an exciton in a rather shallow state.

When the temperature is raised above 2 K, the behaviour of the COL excitation spectrum is very similar to the case of emission [20]. Accordingly, thermal quenching of the 2.1774 eV line is also evident in PLE in the same temperature range, i.e. below 45 K [20]. Similarly all other sharp lines in Fig. 2 below 2.31 eV disappear in the same temperature range (≈ 45 K), as expected if they correspond to excited BE configurations. As in emission the broad phonon background above 2.18 eV, remains essentially unchanged around 45 K, but even the strong rise above 2.21 eV is observed at these temperatures. The behaviour with rising temperature strongly suggests that the A_0 state couples in a qualitative similar manner to the low energy phonon modes which promote the temperature quenching of the sharp line structure [20]. This is also consistent with the finding in PL spectra that strong electronic quenching effects only occur at significantly higher temperature.

In an attempt to determine the nature of the observed structure in the PLE spectrum (Fig. 2), magneto-optical experiments were performed in magnetic fields up to 3.5 T. In agreement with earlier data the BE ground state at 2.1774 eV shows a splitting into a very slightly unsymmetric

triplet, and the splitting is almost isotropic for different crystallographic orientations of the magnetic field direction. Therefore a definite determination of the symmetry axis for the COL defect from orientational dependence of Zeeman splitting has not been obtained. A similar splitting into three components was observed for the lines $B_1 - B_3$, consistent with the identification of these lines as low energy phonon replicas of the 2.1774 eV electronic transition (Fig. 4a). All higher energy lines of reasonably low spectral width in the PLE spectrum were also investigated in a magnetic field. It was found that no splitting was detectable for any of these, as can be seen in Fig. 4b. The finite width of these lines at zero field does not rule out a small splitting in most cases, but any such splitting seems to be about an order of magnitude smaller for the rather narrow lines $A_0 - A_2$ and $A_9 - A_{11}$ (Fig. 4b) than the splitting observed for the 2.1774 eV line and its phonon replicas $B_1 - B_3$. The simplest rationalization of these data is that these lines in fact are all of singlet character. This is consistent with the above classification of the sharp features $A_0 - A_{12}$ as corresponding to the singlet $J=0$ state A_0 and phonon replicas of transitions to this state.

V. Discussion

V:1. The identity of the COL centre in relation to optical data

In early work on the COL-centre the interpretation of data was focused around the assumption that the centre was a $V_{Ga} - O_P$ complex [17-19]. Later it became clear that neither V_{Ga} nor O_P were necessarily involved in the centre [8,9]. Instead it was shown to involve Cu, since isotope shifts were observed in some phonon replicas of the COL-emission upon comparing spectra from samples doped with Cu^{63} and Cu^{65} respectively [5]. The L_1

replica was observed to shift downwards in energy about 0.15 meV when Cu^{63} was replaced by Cu^{65} . The corresponding shift for the modes L_2 and L_3 was 0.3 meV and for L_8 0.5 meV. Doping experiments involving different shallow dopants (S, Si, Te, N, Zn) have failed to establish any relationship between the observation of the COL emission and the abundance of such shallow dopants. An associate involving Cu and shallow donors or acceptors is therefore less probable for the identity of this centre. Consequently the basic conclusion from doping studies is that Cu is involved, and also that it seems natural to suggest an identity of the COL defect based on Cu atoms alone.

The identification of the lowest BE transition at 2.1774 eV as a nearly isotropic spin triplet [19] necessarily limits the choice of possible defect configurations to a centre where no unpaired spin is present in the final state of the transition. This fact immediately sorts out all possible cases of neutral acceptor configurations, where at least one extra particle would be present in the absence of the exciton [28]. In addition such a configuration would lead to strong Auger effects upon recombination of the exciton, while the long decay time of the emission ($\approx 100 \mu\text{s}$) proves that Auger effects are not important for the COL recombination. Another possibility is an ionized acceptor-like centre, where no spin would be present in the final state. The strong appearance of the COL emission in both n-type and p-type GaP is a strong argument against the ionized centre model, since the same charge state would hardly dominate in both cases. In addition, excitons bound to ionized centres seem not to have been observed in GaP. We are therefore left with the neutral isoelectronic centre as the only reasonable identity for this Cu-related defect. In the case of an isoelectronic centre there should be no extra particle in the final state of the transition, which can take part in Auger processes. Bound exciton states of a triplet-singlet character are also

possible, e.g. in a strong axial field produced by the local strain between the atoms of a complex [15,29].

The previous discussion has ruled out all possible models of the defect based on an isolated substitutional Cu_{Ga} acceptor, since in that case two holes are present on the defect if neutral. We note that for tightly bound excitons we also have to rule out the presence of a d-hole in the final state of the COL transition, since such a hole would experience a strong overlap with the hole involved in the exciton, and thus be sensitive to Auger processes under recombination. The presence of the COL emission in both n-type and p-type GaP is also a strong argument against the involvement of a 3d-hole, with the corresponding acceptor state within the bandgap. Therefore even a two-atomic Cu-complex such as $\text{Cu}_{\text{Ga}}-\text{Cu}_{\text{I}}$ with Cu_{Ga} in a $3d^9$ configuration is insufficient as a candidate for the COL centre. This model would simply create a single axial acceptor, which would not be isoelectronic. It is necessary to involve two interstitial Cu atoms, each acting as singly charged donor with the 4s electron as the donor electron, to compensate the double Cu_{Ga} acceptor and create a neutral isoelectronic associate in the same sense as e.g. the Zn-O complex in GaP [6].

In the zincblende structure there are two types of interstitial sites, which impurity atoms can occupy without forming bonded configurations. The rather large tetrahedral site is surrounded by four atoms of the same type, either Ga atoms or P atoms in GaP. Between two tetrahedral sites of different sublattice type, there is a hexagonal site in the centre of a six-membered ring, with three atoms of each kind [30]. The most probable arrangement for the COL centre seems to be a central Cu_{Ga} and two interstitial Cu atoms on each side. Then the Cu_{I} atoms can either occupy tetrahedral sites or hexagonal ones. The former arrangement is linear in the $\langle 100 \rangle$ -direction, whereas the latter would lead to a slightly nonlinear configuration, with an overall symmetry approximately $\langle 110 \rangle$. No ODMR

signal has been detectable for the COL emission, indicating a strong thermalization in the initial triplet state of the transition. Since the isotropic nature of the transition does not provide any reliable information on the defect symmetry from Zeeman measurements either, we cannot exclude any of the two arrangements of Cu atoms at the present stage. In diamond and Si the hexagonal site has been calculated to have lower energy than the tetrahedral one for self-interstitials, but no such information for the zincblende structure is known to the authors [30].

The complicated phonon coupling to the COL transitions provides information on the defect structure, which seems to support the suggested model of three Cu atoms given above. The strong L_8 mode of 27.1 meV (Fig. 1) is assigned to a perturbed LA mode involving the motion of Cu_{Ga} alone [31]. This is supported by the large isotope shift of this mode when replacing Cu^{63} by Cu^{65} , and the fact that only the LA(X) mode involves selective motion of the Ga sublattice. Vibrations of Cu_{Ga} along the $\langle 100 \rangle$ -direction could then produce this strongly localized resonance mode. The three complex low energy modes $L_1 - L_3$ also show large isotope shifts, characteristic of pure Cu motion. In view of the low energy of these modes and the additional degrees of freedom of interstitial atoms compared with substitutional ones, the modes $L_1 - L_3$ are understood in terms of vibrations of the Cu_I atoms. The vibrational modes involving the motions of Cu_I are classified according to parity under reflections which interchange the two Cu_I atoms. The even parity modes then yield the observed replicas $L_1 - L_3$ [20,31].

At the rather high temperatures where the COL centres are formed (900 - 1100 °C), we may assume that a sufficient amount of Ga vacancies (V_{Ga}) is present to provide the prestage of Cu_{Ga} substitutes. It is assumed that Cu diffuses quite rapidly at these temperatures by an interstitial mechanism [31], which should provide a large amount of Cu_I donors. The

pairing of the charged species $(\text{Cu}_{\text{Ga}})^{2-}$ and Cu_{I}^{+} at the diffusion temperature into a neutral isoelectronic complex then would be expected. On rapid quenching down to room temperature these complexes will be frozen in, and they are expected to dominate the impurity-related PL spectra from such Cu-diffused undoped GaP, as observed. The failure to associate with shallow donors can be explained by the much lower mobility of these species.

V:2 Electronic structure of the COL centre

The excitation spectra of the COL-centre, which were measured for the first time in this work, provide important information on excited bound exciton states, relevant for the identification of the centre. Previous data on excited states for relatively deep bound excitons are scarce, however, and essentially limited to simpler cases of isoelectronic traps, such as NN-pairs [27] or Bi [33] in GaP, where only one of the particles is deeply bound. For the molecular isoelectronic traps such as Cd-0 [23-25] or Li-Li-0 [26], low lying electronic states within a few meV of the BE ground state have also been observed. In the case of the NN-pairs a well defined hydrogenic series of s-like excited states for the holes in the Coulomb field of the electron was observed [27], as expected from the Hopfield-Thomas-Lynch model [34]. In addition some evidence was found for the observation of excited states of the electrons in the case of nearest neighbour NN_1 -pairs [27].

In the case of the COL centre a comparison with the simple model with one particle loosely bound in the Coulomb field of the other (tightly bound) particle might be of limited value, since we believe that both the electron and hole are rather tightly bound to the COL centre. The higher BE states observed for the COL centre are instead analogous to the cases of molecular traps such as Cd-0 or Li-Li-0 [23-26], with the important

difference that the axial field and exchange splittings are about an order of magnitude larger for the COL case.

The suggested identity of the COL centre has the natural consequence that the Cu atoms are in a strong compressive strain field, since two interstitial Cu atoms are accommodated locally. This is in contrast to e.g. the substitutional Cd-O complex in GaP, where the small size of the O_p atom creates a local tensional strain field [23-25]. The observed spin triplet for the BE ground state implies strongly quenched spin-orbit effects for the hole states involved, which can be understood as a direct consequence of the strong axial crystal field [15]. In the absence of axial field the p-like Γ_{15} valence band states of the GaP host are split into a $j=3/2$ Γ_8 band and $j=1/2$ Γ_7 split-off band, due to the spin-orbit interaction in cubic symmetry [35]. This splitting amounts to 82 meV in GaP at the Γ point. An axial strain field lowers the symmetry and splits the fourfold degenerate Γ_8 hole state into a $|3/2, 3/2\rangle$ state and a $|3/2, 1/2\rangle$ state with the usual $|j, m_j\rangle$ notation of total angular momentum (j) and magnetic quantum number (m_j). Bound exciton states derived from these hole states split in a similar way.

Strain induced mixing between the basic hole states $|3/2, 1/2\rangle$ and the split off state $|1/2, 1/2\rangle$ occurs, as symmetry allows coupling of states with the same $|m_j|$ value. These states can be written as

$$|1/2, 1/2\rangle = \frac{1}{\sqrt{3}} [p_0\uparrow - p_+\uparrow]$$

$$|3/2, 1/2\rangle = \frac{1}{\sqrt{6}} [2p_0\uparrow + p_+\uparrow]$$

where p_0 and p_+ are the orbital angular momentum components relative the symmetry axis of the defect, and $\uparrow$ indicates the spin direction. Compressive axial strain field increases the binding energy of the $|m_j| = 1/2$ holes. A very strong axial field of this sign eventually decouples the

spin and orbital angular momentum of the $|m_j| = 1/2$ hole states, leaving the hole as a pure spin particle ($s = 1/2$) in the ground state of the bound holes. In Fig. 5 is shown a level diagram illustrating this situation. The axial field is shown much stronger than the spin-orbit interaction, which is expected to be reduced below the Δ_{SO} of the GaP lattice, or even show a negative sign compared to the host. This may occur through hybridization of the hole wave function with the d-orbitals of Cu, which shows an inverted sign of the spin-orbit splitting [36]. In any case the axial strain field is shown to split the threefold orbitally degenerate valence band states Γ_{15} into a p_0 state at highest hole binding energy and a two-fold degenerate $p_{\pm}$ state. This latter state splits in two states when including the smaller spin-orbit interaction. The lowest bound exciton states are formed by coupling an electron with the pure spin hole, given a $J=1$ spin triplet and a $J=0$ singlet state, with the triplet lowest. Transition to these states correspond to the B_0 line ($J=1$) and the A_0 line ($J=0$) in Fig. 2. The electron-hole exchange interaction will split off the $J=0$ state with the antiparallel spin configuration, since the involved particles have opposite charge. The $p_{\pm}$ hole states split-off by the axial field give rise to higher excited BE states, of which one could probably be identified with the strong C_0 line, 109 meV higher than the lowest BE state B_0 (Figs. 2 and 5).

This picture of the electronic configuration for the COL bound exciton is supported by the experimental data. Zeeman data show essentially isotropic magnetic splittings, in agreement with a quenching of the hole angular momentum in a strong axial field. Further, there is a rather large strain-induced splitting $D = 0.15$ meV of the B_0 line in zero magnetic field. This is an evidence for the effect of a strong strain field on a spin triplet, which should be nearly unaffected by the crystal field. The long decay time of the COL emission is expected for a spin forbidden transition

from the $J=1$ triplet to the $J=0$ ground state, which violates the spin selection rule $\Delta S=0$ (i.e. $\Delta J=0$ with our notations). The much larger total oscillator strength of the $J=0$ transition A_0 (including the phonon wing) is also understood in terms of this spin selection rule.

The formation of the COL bound exciton upon optical excitation can be viewed as a transfer of charge from a Cu_{Ga} bond to the Cu_{I} atoms. The BE wave function will be a mixed configuration of all possible charge transfer processes. The Cu_{I} atoms share the electron wave function in a similar way as in the H_2^+ molecule, forming the donor-like part of the complex. The hole is bound to the Cu_{Ga} acceptor-like part. All three Cu atoms have filled d-shells ($3d^{10}$). Since both the hole and the electron are tightly bound to the isolated parts of the complex, a strong localization of the hole and electron wave functions is to be expected for the BE. This has several important consequences for the electronic properties of the COL centre. The most obvious effect is a reduction of electron-hole binding energy to about 0.17 eV through Coulomb repulsion (the Cu_{Ga} acceptor binding energy is believed to be about 0.5 eV [4,7], the Cu_{I} donor binding energy is unknown, but expected to be larger than 0.1 eV). As pointed out previously, the absence of Coulomb excited states also indicates a strong binding for both particles in the bound exciton states. The strong electron-hole overlap in the vicinity of the central cell of the COL defect will then produce the unusually large J-J splitting energy Δ_{JJ} of 23.2 meV. This is not the case for previously studied molecular isoelectronic traps, where one particle is loosely bound, as e.g. the Cd-O BE in GaP, with hole binding energy of about 35 meV. Consequently these BE only show small exchange splittings. As a comparison, a similar order of the lowest BE states as well as an even larger J-J splitting between the $J=0$ and $J=1$ states is found in another deeper isoelectronic Cu complex, with lowest BE line at 1.911 eV [37].

VI. Conclusions

The electronic properties of the COL centre in GaP, described in this paper are of basic interest, since they establish a new class of isoelectronic defects with properties dramatically different from previously studied isoelectronic traps of the single substitutional type or the molecular pair type [15]. The identification of the COL centre as a defect containing only Cu is supported by evidence from variation in doping conditions, since the COL spectrum was not found to be influenced by any additional dopants besides Cu. Further the COL spectrum seems to be strong in both n-type and p-type GaP, provided that proper Cu diffusion temperatures and rapid quenching is employed. No evidence in addition to these circumstances and the optical spectra themselves could be obtained to support this identification, since no EPR signal was observed for Cu in GaP [13], and no ODMR signal related to the COL spectrum could be observed either. From the evidence presented, a $\text{Cu}_\text{I}-\text{Cu}_{\text{Ga}}-\text{Cu}_\text{I}$ molecular defect complex appears to be the natural identification of the COL centre, which was in the early literature misinterpreted as a $\text{V}_{\text{Ga}}-\text{O}_\text{P}$ defect [23-25]. Three Cu atoms are necessary in this case to create the neutral isoelectronic associate required to explain the spectroscopic data. The natural positions for the Cu_I atoms are either the nearby tetrahedral interstitial sites on each side of Cu_{Ga} , giving a linear $\langle 100 \rangle$ -oriented defect, or the hexagonal interstitial sites resulting in a nonlinear orientation with approximately $\langle 110 \rangle$ symmetry.

The presence of a strong axial strain field at the defect is expected in this case, since two extra interstitial Cu atoms are accommodated locally in the lattice. This has profound effects on the electronic bound exciton states. The strain field decouples the angular momentum components of the basic hole states, leaving pure spin states, from which the lower $J=1$ and

$J=0$ components of the BE are formed. Hybridization of the hole wavefunction with the Cu 3d-orbitals is believed to promote a reduction of the hole spin-orbit splitting Δ_{SO} well below the value of 82 meV, appropriate for GaP, so that the main factor determining the electronic level structure of the BE is the local strain field.

Another unique feature expected for the $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ defects is a rather strong binding for both electronic particles in the complex. This is unlike the case of substitutional isoelectronic defects and also previously studied substitutional molecular traps in GaP, where one of the particles is always found to be quite loosely bound, even for the deep centres [15]. In agreement with this idea we do not observe any orbitally excited states of one of the particles in the Coulomb field of the other, as was seen e.g. with the NN pairs in GaP [27]. The large J-J splitting of 23.2 meV between the ground state triplet B_0 at 2.1774 eV and the singlet A_0 at 2.2006 eV is explained by a strong overlap of the electron-hole pair, where the particles have comparable binding energies. This is also an extraordinary feature, since J-J splittings are found to be typically of the order 2 meV for excitons bound to isoelectronic centres in GaP, and only slightly larger values have been found in alloys [38]. Since the binding energies of the isolated Cu_I donors have not been established, no detailed estimates of the fractional energies involved in binding of both particles can be made.

A typical feature for this isoelectronic defect seems to be that the higher $J=0$ BE state has a stronger total oscillator strength than the $J=1$ ground state, mainly due to a much stronger phonon coupling in the $J=0$ state. This is understood in terms of the spin selection rule $\Delta S=0$, according to which transitions between a spin triplet and a $J=0$ ground state are forbidden. The larger oscillator strength associated with the $J=0$ excited

BE state is even more pronounced in another deeper Cu-related bound exciton with ground state at 1.911 eV [37]. The peculiarities in phonon coupling to the COL centre will be described separately [20], but the observation of several low energy quasi-localized modes is one piece of evidence for the presence of interstitial Cu_I atoms in this centre. Studies on the properties of a large number of additional Cu-related defects, are continued in order to clarify the intriguing role of Cu in connection with defect related properties of GaP.

Acknowledgments

The authors are grateful to P.-O. Holtz for providing some results on temperature dependence and doping conditions prior to publication. Also we thank S. Jeppesen for making some of the Cu-diffusions and B.C. Cavenett, S. Depinna and N. Killoran for discussions on the identity of the COL defect.

References

1. J.W. Allen and R.J. Cherry, J. Phys. Chem. Solids 23, 509 (1962).
2. H.G. Grimmeiss and M.O. Ottosson, phys. stat. sol. (a) 5, 481 (1971).
3. R. Olsson, phys. stat. sol. (b) 46, 299 (1971).
4. B. Monemar, J. Luminescence 5, 472 (1972).
5. D.R. Wight, J.W.A. Trussler and W. Harding, Proc. XIth Int. Conf. on Semiconductors, p. 1091, Warsaw 1972.
6. P.J. Dean, J. Luminescence 7, 51 (1973).
7. H.G. Grimmeiss and B. Monemar, phys. stat. sol. (a) 19, 505 (1973).
8. E. Fabre and R.N. Bhargava, Appl. Phys. Lett. 24, 322 (1974).
9. B. Wessels, J. Appl. Phys. 47, 1131 (1976).
10. P.O. Fagerström, H.G. Grimmeiss and H. Titze, J. Appl. Phys. 49, 3341 (1978).
11. B. Monemar, J. Luminescence 5, 239 (1972).
12. H.G. Grimmeiss, B. Monemar and L. Samuelson, Solid State Electron. 21, 1505 (1978).
13. J. Schneider, private communication, 1979.
14. L.L. Chase and D. Walsh, Inst. Phys. Conf. Ser. 43, 533 (1979).
15. P.J. Dean and D.C. Herbert, in "Topics in Current Physics", Vol. 14, "Excitons", Ed. K. Cho (Springer Verlag, 1979), pp. 55-182.
16. F. Willmann, D. Bimberg and M. Blätke, Phys. Rev. B 7, 2473 (1973).
17. R.N. Bhargava, S.K. Kurtz, A.T. Vink and R.C. Peters, Phys. Rev. Lett. 27, 183 (1971).
18. G.M. Blom and R.N. Bhargava, J. Crystal Growth 17, 38 (1972).
19. P.J. Dean, Solid State Commun. 9, 2211 (1971).
20. H.P. Gislason, B. Monemar, P.-O. Holtz, P.J. Dean and D.C. Herbert, unpublished.
21. B. Monemar and L. Samuelson, Phys. Rev. B 18, 809 (1978) and Solid State Commun. 26, 165 (1978).

22. R. Bindemann, H. Fischer and K. Kreher, *phys. stat. sol. (a)* 43, 529 (1977).
23. T.N. Morgan, B. Welber and R.N. Bhargava, *Phys. Rev.* 166, 751 (1968).
24. C.H. Henry, P.J. Dean and J.D. Cuthbert, *Phys. Rev.* 166, 754 (1968).
25. J. Van W. Morgan and T.N. Morgan, *Phys. Rev. B* 1, 739 (1970).
26. P.J. Dean, *Phys. Rev. B* 4, 2596 (1971).
27. E. Cohen and M.D. Sturge, *Phys. Rev. B* 15, 1039 (1977).
28. P.J. Dean, R.A. Faulkner, S. Kimura and M. Illegems, *Phys. Rev. B* 4, 1926 (1971).
29. P.J. Dean, W. Schairer, M. Lorenz and T.N. Morgan, *J. Luminescence* 9, 343 (1974).
30. J.W. Corbett and J.C. Bourgoin, in "Point Defects in Solids", Ed. J.H. Crawford, Jr. and L.M. Slifkin (Plenum Press, New York, 1975), Ch. 1.
31. P.J. Dean, B. Monemar, H.P. Gislason and D.C. Herbert, *Proceedings of the ICL Conference, Berlin* (1981).
32. N. Magnea, D. Bensahel, J.L. Pautrat and J.C. Pfister, *phys. stat. sol. (b)* 94, 627 (1979).
33. R.A. Faulkner and P.J. Dean, *J. Luminescence* 1,2, 552 (1970).
34. J.J. Hopfield, D.G. Thomas and R.T. Lynch, *Phys. Rev. Lett.* 17, 312 (1966).
35. D. Long, in "Energy Bands in Semiconductors" (John Wiley, 1968), p. 101.
36. D.J. Robbins, D.C. Herbert and P.J. Dean, *J. Phys. C* 14, 2859 (1981).
37. H.P. Gislason, B. Monemar, P.J. Dean, D.C. Herbert, S. Depinna, B.C. Cavenett and N. Killoran, unpublished.
38. D.J. Wolford et al., *Proc. Semicond. Conf.* 1980.

Table I a

EMISSION			
Notation	Phonon energy eV	Energy difference meV	Interpretation
L_0	2.1774	0	$J=1$ triplet
L_1	2.1721	5.3 ± 0.1	L_1^A 4.7 ± 0.1
L_2	2.1706	6.8 ± 0.1	L_2^A 6.4 ± 0.1
L_3	2.1686	8.8 ± 0.1	L_3^A 8.1 ± 0.2
L_4	2.1654	12.0 ± 0.2	
L_5	2.1639	13.5 ± 0.2	
L_6	2.1631	14.3 ± 0.3	
L_7	2.1593	18.1 ± 0.5	
L_8	2.1503	27.1 ± 0.2	LA perturbed
L_9	2.1449	32.5 ± 0.3	
L_{10}	2.1437	33.7 ± 0.3	
L_{11}	2.1418	35.6 ± 0.3	
L_{12}	2.1377	39.7 ± 0.3	
L_{13}	2.1320	45.4 ± 0.3	TO_Γ
L_{14}	2.1273	50.1 ± 0.3	LO_Γ
L_{15}	2.1224	55.0 ± 0.7	2LA
L_{16}	2.1004	77.0 ± 1.0	

Table I b

ABSORPTION			
Notation	Photon energy eV	Energy difference from B_0 meV	Interpretation
B_0	2.1774	0	J=1 triplet
B_1	2.1819	4.5	
B_2	2.1834	6.0	
B_3	2.1861	8.7	
A_0	2.2006	23.2	J=0 singlet
A_6	2.2034	26.0	$A_0 + 2.8$ meV or $B_0 + 26$ meV (B_8)
A_1	2.2056	28.2	$A_0 + 5.0$ meV
A_2	2.2068	29.4	$A_0 + 6.2$ meV
A_3	2.2084	31.0	$A_0 + 7.8$ meV
A_4	2.2100	32.6	
A_5	2.2134	36.0	$A_0 + TA(X)$
A_6	2.2199	42.5	$A_2 + TA(X)$
A_7	2.2267	49.3	$A_0 + 26.1$ meV
A_8	2.2327	55.3	$A_2 + 25.9$ meV
A_9	2.2413	63.9	$A_0 + 40.7$ meV
A_{10}	2.2450	67.6	
A_{11}	2.2456	68.2	
A_{12}	2.2493	71.9	
C_0	2.2864	109.0	
C_2	2.2932	115.8	$C_0 + 6.8$ meV
C_5	2.3004	123.0	$C_0 + 14$ meV

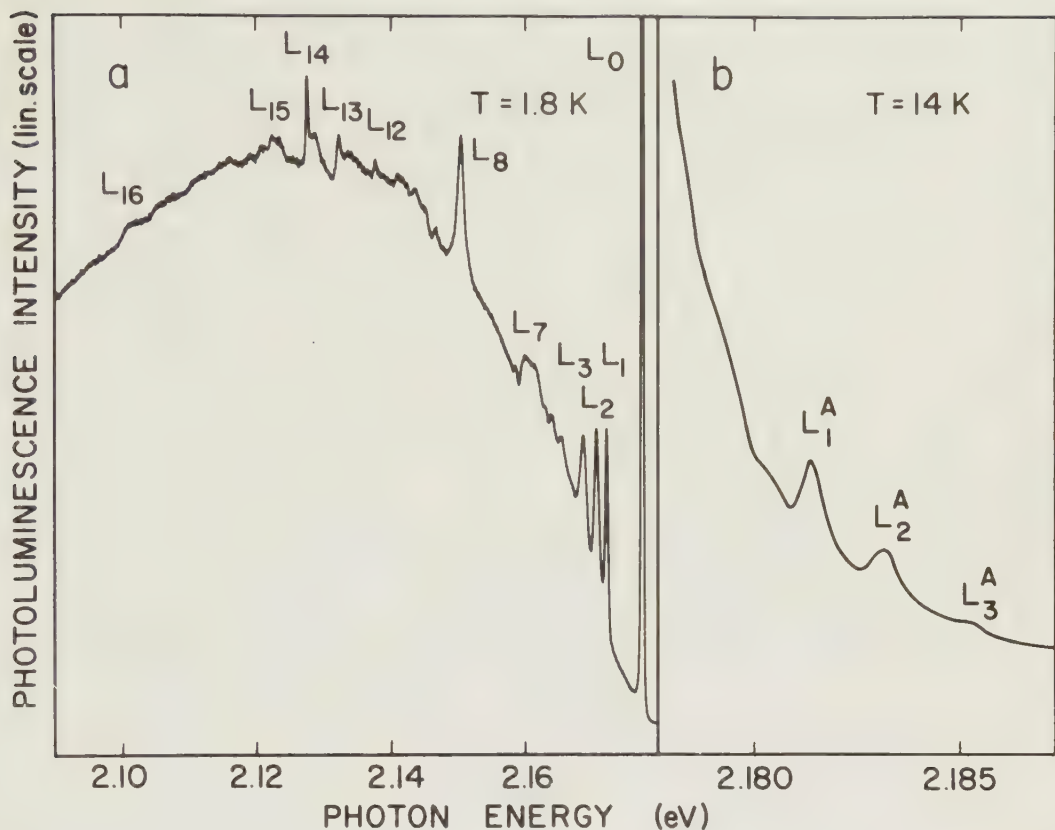


Fig. 1a. Photoluminescence spectrum for the COL bound exciton at 1.8 K for a Cu-doped GaP epitaxial layer, excited with a 5145 Å Ar⁺-laser line. The J=1 electronic transition L_0 occurs at 2.1774 eV. Energies of phonon replicas labelled L_1 - L_{16} are listed in Table 1.

Fig. 1b. High energy part of the COL photoluminescence spectrum at 14 K for the same crystal as in Fig. 1a. At this temperature anti-Stokes phonon replicas L_1^A - L_3^A are clearly observed. The phonon energies in the excited vibronic state are somewhat reduced compared with the corresponding phonon replicas L_1 - L_3 in the ground state (see Table 1).

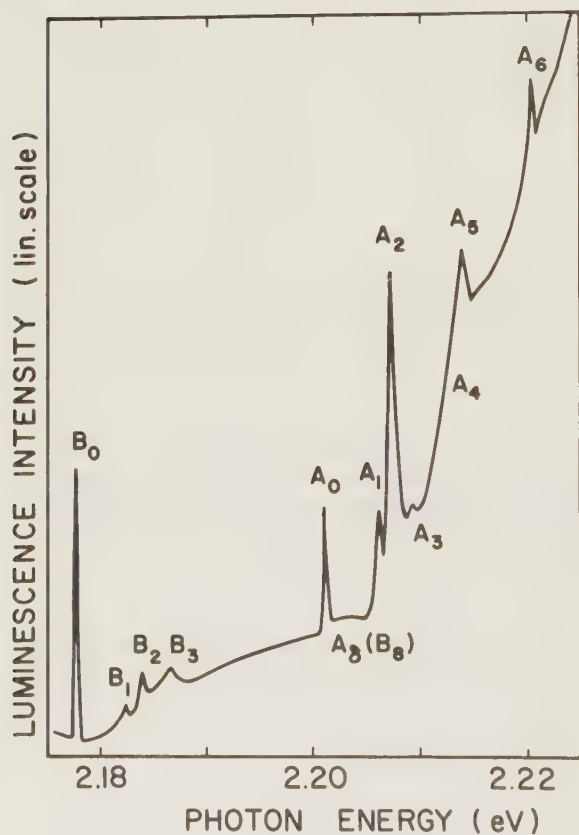
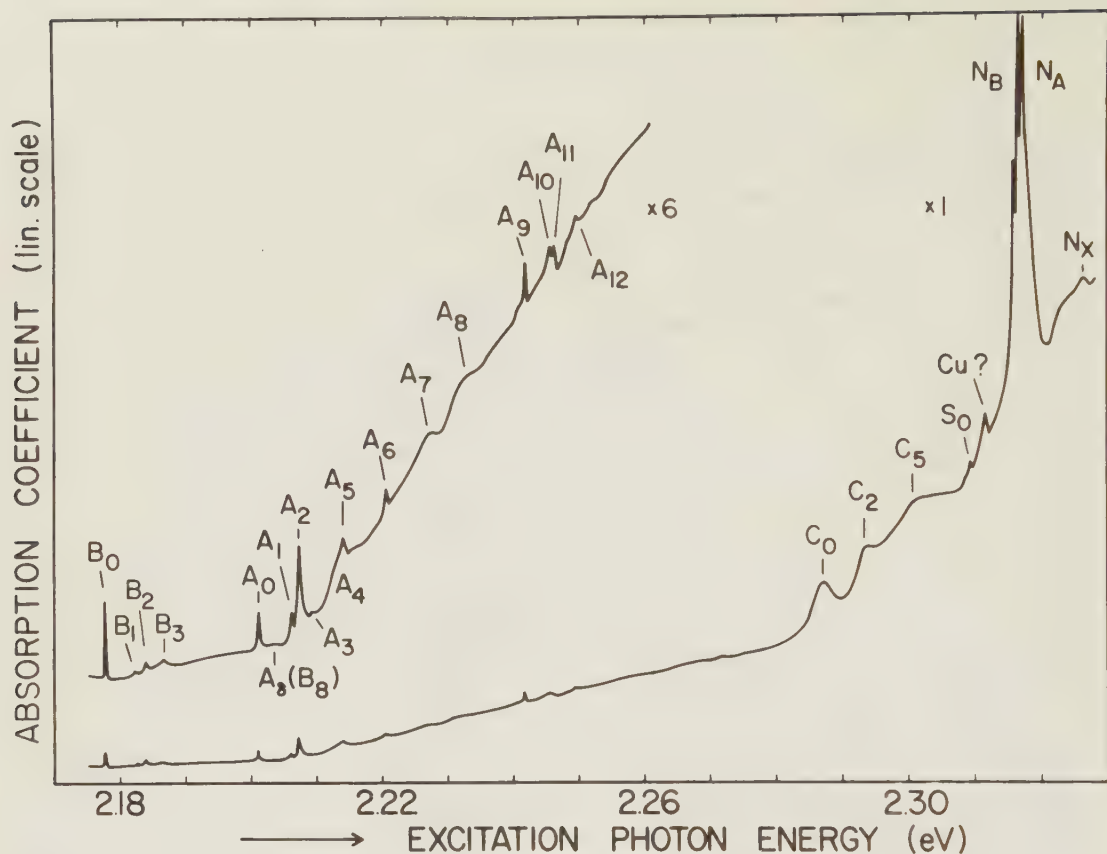


Fig. 2. Excitation spectrum of the COL emission at 2 K obtained with tuneable dye laser excitation with the detection wavelength set to 5870 Å. The spectrum shows the J=1 electronic transition B₀ at 2.1774 eV and three discrete low energy phonon replicas B₁-B₃ corresponding to the L₁-L₃ replicas in emission. The three peaks A₁-A₃ above the J=0 electronic transition A₀ at 2.2006 eV are the same phonon modes with different relative strength. For interpretation see Table 1.

Fig. 3. Low energy part of the excitation spectrum in Fig. 2. Here the electronic transitions B₀ (J=1) and A₀ (J=0) are shown in more detail together with their low energy phonon replicas B₁-B₃ and A₁-A₃ respectively. Most of the slowly varying background is subtracted.

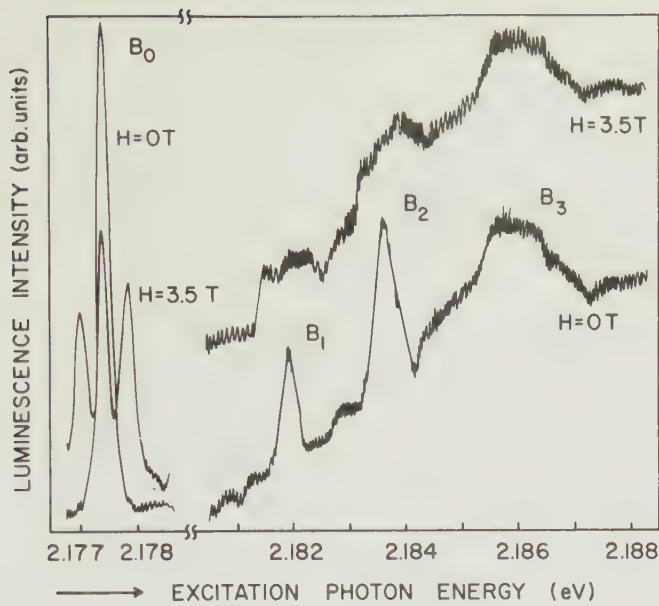


Fig. 4a. Excitation spectrum of the $J=1$ electronic transition B_0 and its low energy phonon replicas. The spectrum is measured in magnetic field $H=3.5\text{ T}$ in the Voigt configuration with $H//[110]$. The zero-field spectrum is shown for comparison. The B_0 line splits into a slightly anisotropic triplet. The similar splitting of the $B_1 - B_3$ components is consistent with the identification of these as phonon replicas of B_0 .

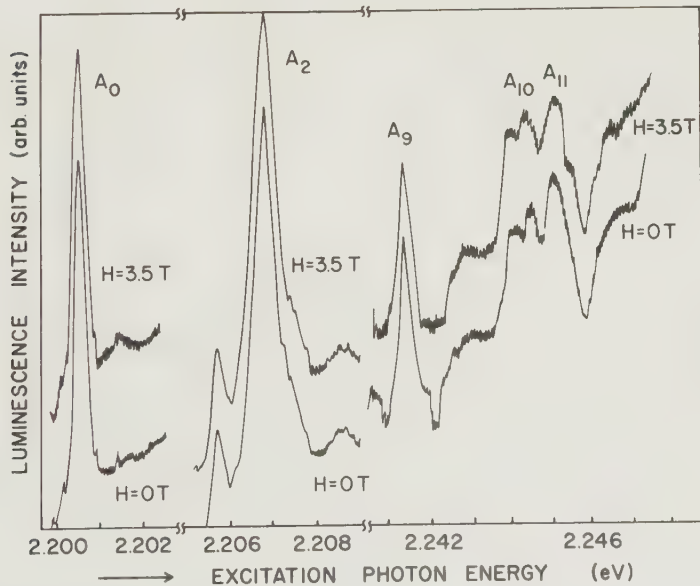


Fig. 4b. Excitation spectrum of the $J=0$ electronic line A_0 and its strong phonon replica A_2 in magnetic field as above. No splitting is observed when comparing with the zero-field spectrum. The peaks $A_9 - A_{11}$ are also unsplit in magnetic field. They are consequently classified as phonon replicas of A_0 .

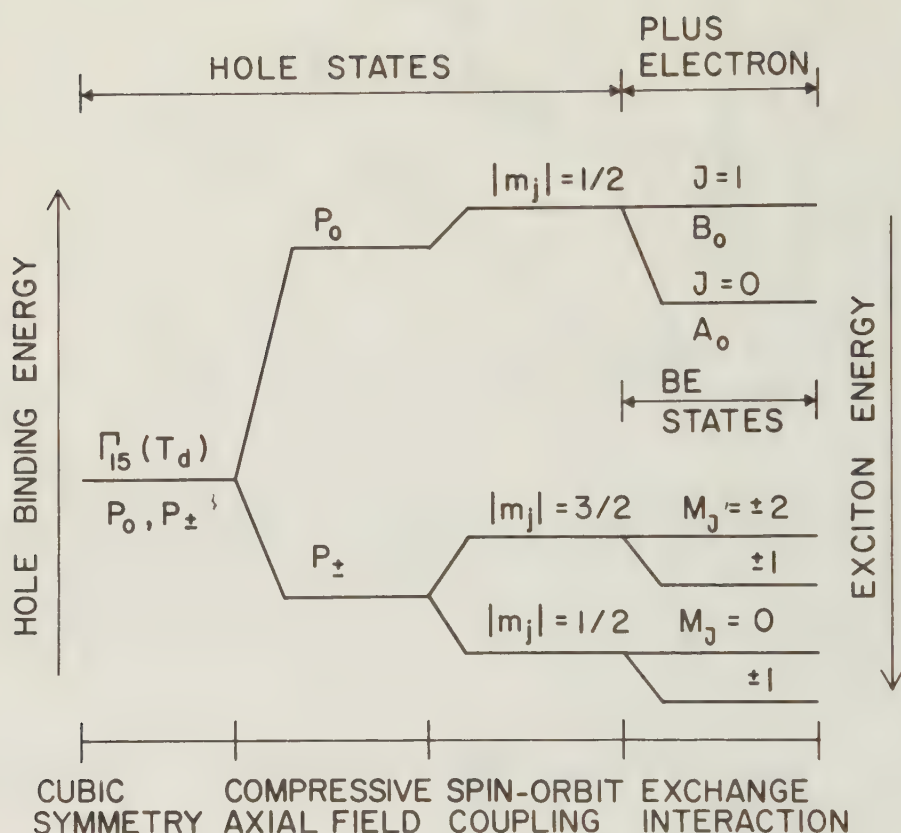


Fig. 5. Schematic model of energy levels for the COL bound exciton states, showing the relative influence of the different coupling mechanisms. As shown to the left, the axial field is assumed to be very strong and to have the sign of a local compression, due to the large ionic radii of the Cu_I atoms involved. This sign of the crystal field creates a splitting of the p-like hole state Γ_{15} into the hole states p_0 at highest hole binding energy and the split-off state $p_{\pm}$. The coupling of a hole in the pure spin state p_0 to an electron leads to the observed singlet-triplet pair for the bound exciton. The pure spin triplet $J=1$ is the BE ground state at 2.1774 eV (B_0), while the $J=0$ singlet (A_0) is split off 23.2 meV by the exchange interaction. Bound exciton states from the weakly bound $p_{\pm}$ hole states are considered responsible for the high energy transition C_0 in Fig. 2. Exchange and spin-orbit splittings involving these relatively weakly bound $p_{\pm}$ holes are probably less than shown schematically here.

Thermal behaviour of the Cu-related COL bound exciton in GaP

H.P. Gislason, B. Monemar and P.O. Holtz

University of Lund, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

P.J. Dean and D.C. Herbert

RSRE, Gt Malvern, Worcs WR14 3PS, England

Abstract

New experimental results from photoluminescence (PL) data are presented for the Cu-related COL centre in GaP. The PL spectrum shows a sharp electronic line at 2.1774 eV at 2 K, together with a very complicated phonon wing from interaction with continuum modes as well as a large number of rather sharp in-band resonance modes. The phonon coupling causes the electronic line to disappear completely above 45 K, while the entire COL emission is thermally quenched by an electronic process above 140 K. The thermal activation energy deduced from this electronic quenching is consistent with the thermal emission of the exciton as a single entity. A qualitative estimate of the contributions of discrete and continuum phonon modes to the quenching of the zero-phonon line is also presented. The presence of a low frequency mode of 2.6 meV makes a quantitative evaluation difficult, since this phonon mode is found to couple only in the excited vibronic state, when thermally excited. Comparison between the discrete phonon energies on the anti-Stokes wing and those obtained from previously reported absorption measurements shows that these agree within experimental accuracy. The phonon energies in the excited vibronic state are reduced compared to the values for the ground state, illustrating anharmonic effects in the phonon coupling.

I. Introduction

Several investigations have been published in recent years on defect related properties associated with the common contaminant Cu in GaP [1-7]. A variety of discrete deep levels has been reported with different binding energies, although the identities of the defects causing these levels have not yet been established [1-7]. In some cases not even the presence of Cu in the defect was confirmed. The two most commonly observed centres lie 0.5 eV and 0.7 eV above the valence band edge [4,6,7]. These acceptor like levels have been studied with several different measuring techniques. Electrical measurements, such as photoconductivity and photocurrent [6], have given results for binding energies consistent with purely optical measurements such as photoluminescence and photoluminescence excitation [7] performed on bulk material. The optical measurements include the study of excitons bound to different impurity complexes introduced in GaP by Cu-diffusion [1, 8, 9, 10, 11].

Bound exciton spectroscopy with magneto-optical techniques has become a powerful tool of characterizing the defects to which the excitons are bound [12]. Recently, the introduction of tunable dye lasers has greatly improved the possibility of studying weak radiative processes, providing a continuous range of narrow monochromatic excitation energies, utilized e.g. in photoluminescence excitation spectroscopy [13]. The identity of the defects is sometimes most easily deduced with the recently developed technique of optically detected magnetic resonance (ODMR), which has further improved the possibilities of revealing the symmetry of defects involved in luminescence [14]. All these techniques have lately been employed in the study of bound excitons caused by Cu diffusion into GaP [15, 16, 17].

The aim of this renewed interest in Cu-related excitons in GaP is to establish the relation between Cu-doping conditions and the different

types of complexes introduced in GaP. In the investigation reported here the COL emission with an electronic line at 2.1774 eV has been studied. In earlier work this emission was ascribed to a $V_{Ga}-0_p$ complex [8-10] but later this interpretation was found to be incorrect [3]. In the present study the COL centre is found to be independent of other impurities than Cu, consistent with earlier isotope measurements [3]. A model of the centre as being a $Cu_I-Cu_{Ga}-Cu_I$ complex has been proposed [15].

The observed low temperature emission and photoluminescence excitation (PLE) spectra are related to the electronic states of an exciton bound to an isoelectronic axial defect. The lowest state of this bound exciton is a $J=1$ triplet at 2.1774 eV, while a $J=0$ singlet at 2.2006 eV, i.e. 23.2 meV above the lowest state, was deduced from PLE measurements [15]. This J - J splitting is about a factor of ten larger than usually observed. Consequently the energy difference between the singlet and the triplet is too large for the singlet to become thermally populated even at rather high temperatures, and transitions from this state are therefore not seen in emission.

In this paper we provide complementary data on the COL emission, measured at different temperatures. The purpose is to reveal the temperature dependence of both the total emission intensity and the intensity of the electronic line. From the former we deduce the binding mechanism of the exciton to the defect, and from the latter the importance of phonon coupling in quenching the intensity of the electronic line is inferred.

The coupling of electronic and vibrational properties of point defects in crystals has been studied during a long time, particularly for insulators [18-21]. Several theoretical approaches have been made to the nature of the vibrational sidebands associated with an electronic transition at a defect, as well as to the properties of the electronic line itself. This includes the behaviour of the line at elevated temperatures. The work in

this field is summarized in several review articles [18-21]. No qualitative difference exists between these treatments and those appropriate for semiconductors, hence the general formalism [18] is very helpful in analysing the defect-related vibrational spectra of semiconductors as well. The details of the vibrational coupling are unusually complicated for the case of the COL centre in GaP. Therefore a quantitative approach to the interaction between lattice vibrations and electronic transitions will not be attempted. Instead we employ the theoretical framework in a more qualitative way to deduce the relative importance of different vibrational modes active in the total vibronic transition.

In the following section, Section II, a brief description of the experimental procedure is given. A discussion on the doping methods used to introduce and enhance the COL emission is included.

Section III contains experimental results from photoluminescence measurements at temperatures ranging from 1.6 K towards room temperature.

In Section IV we relate the temperature dependence of the COL emission to the vibrational properties of the disturbed lattice. Both contributions of continuous acoustic bands and discrete localized modes of impurity-induced vibrations will be considered.

II. Experimental techniques and samples

Photoluminescence measurements were performed employing an Ar^+ ion laser for intrinsic excitation at 5145 Å, and a cw dye laser for selective extrinsic excitation. Different He cryostates were used for studies of the temperature behaviour of the emission, providing the temperature range of 1.6 K-300 K. A temperature stabilizer guarantees constant temperature, which is even measured independently with a Cr-Au thermocouple.

In this part of the investigation, nominally undoped solution grown epitaxial layers were used. The Cu-diffusion was made at high temperatures (950 - 1050°C) and the samples were rapidly quenched to room temperature after one hour. These crystals show a rather strong COL luminescence with minimal interference with other emissions, since the shallow DA-pair spectra peaking at about 2.2 eV are very weak.

Doping experiments also show that the COL emission is equally strong in crystals with different shallow doping. Both n-type material ($N_D \approx 10^{18} \text{ cm}^{-3}$) and p-type material ($N_A \approx 10^{17} \text{ cm}^{-3}$) give the COL emission of similar intensity as nominally undoped crystals. Also, different types of GaP material, such as epitaxial (LPE) crystals and liquid encapsulated Czochralski (LEC) wafers, give similar spectra.

III. Results

III:1 Low temperature data

The COL emission spectrum shown in Fig. 1 was measured at 1.8 K. It consists of a sharp electronic line at 2.1774 eV accompanied by a prominent phonon assisted sideband extending down to about 1.9 eV. This is similar to previously published data [10], where there also was observed a small residual splitting of about 0.15 meV between the states $M_J=0$ and $M_J=\pm 1$ at zero magnetic field. In our case the narrow electronic line is resolution limited to 0.15 meV at the lowest temperatures, but already at slightly raised temperatures a marked broadening occurs, reflecting a strong coupling to the continuous acoustic phonon bands. The complicated phonon assisted wing is characteristic for the COL emission and illustrates a stronger phonon coupling than is usually the case for other bound excitons with comparable binding energy in GaP [3,12]. The general shape (Fig. 1)

is that of a discrete phonon spectrum superimposed on a smooth phonon related background, which does not clearly reveal the phonon density of states of the GaP host lattice. In cases where the coupling strength is weaker, e.g. for Li-Li-O [22] and Cu-Li [17] in GaP, the one phonon density of states with discrete maxima at the boundaries of the Brillouin zone is more pronounced. On the other hand, discrete structure is nearly absent in the case of the Zn-O centre [23], where the phonon coupling is much stronger.

The rather strong continuum background immediately following the zero-phonon line (Fig. 1) indicates a relatively strong coupling to the low energy parts of the acoustic phonon branches of the crystal. Starting at phonon energies slightly above 5 meV, several rather strong discrete phonon replicas also appear resonant with the acoustic phonon band. The most prominent of these occur at energies 5.3 meV (L_1), 6.8 meV (L_2), and 8.8 meV (L_3) below the electronic line, as shown in Fig. 1 and listed in Table I. In Fig. 2 these three phonon replicas L_1 - L_3 are shown in greater detail, as well as additional very weak ones L_4 - L_6 , which can be assigned to combinations of L_1 - L_3 as listed in Table I. At lower photon energies several rather sharp phonon assisted emission lines occur, corresponding to phonon energies within the one phonon range. The rather broad shoulder L_7 at 18.1 meV is relatively close to the cut off frequency of the TA phonon branch in GaP. This is near the K symmetry point of high phonon density of states in the Brillouin zone [24]. The strong peak L_8 with phonon energy 27.1 meV falls near the density of states maximum of the LA phonon branch. Both these replicas, L_7 and L_8 , are to be considered as quasilocalized in-band resonance modes. The weak structure L_9 - L_{11} in Fig. 2 resembles the low energy modes L_1 - L_3 combined with the L_8 mode, considerably broadened, however. The very weak, but sharp peak L_{12} occurs with a phonon energy of 39.7 meV, thus lying in the gap between the acoustic and

optical phonon branches in GaP [24].

The coupling to TO^Γ is reflected by the L_{13} peak at 45.4 meV, while L_{14} represents the LO^Γ replica at 50.1 meV below the electronic line. The dip in the one-phonon spectrum above the TO^Γ energy often seems to be present in the Cu-related bound exciton spectra [3,17], indicating complex phonon coupling to the modes in the lower part of the optical branch. Beyond the one-phonon region only weak structure can be observed (Fig. 1), because of the weak coupling strength of all the discrete phonon modes (Table I). The L_8 mode has the strongest coupling $p_\lambda = 0.37$, simply taken as its strength compared to the electronic line (see below). Consequently the second replica, L_{15} , of this mode can be seen vaguely.

III:2 PL spectra at elevated temperatures

When the temperature is raised above 2 K new discrete features arise in the COL emission spectrum. Most unexpected is the observation of a new weak and rather broad peak, centered at about 2.4 meV below the electronic line (Fig. 3). On close inspection this peak is split into two components, δ_1 at 2.7 meV and δ_2 at 2.2 meV below the electronic line. Clearly these features involve thermally activated low energy phonon modes, and we find it most natural to associate these two peaks δ_1 and δ_2 with the low energy modes L_1 and L_2 respectively. In this case modes with anti-Stokes energies $\delta_1 - \text{L}_1 = 2.6$ meV and $\delta_2 - \text{L}_2 = 4.6$ meV are present, of which δ_1 does not couple with any noticeable strength to the electronic line in the ground state. In the same temperature range a slight peak δ_3 can be seen on the anti-Stokes side of the zero-phonon line, on top of the continuum anti-Stokes spectrum, displaced about 2.6 meV from the electronic line towards higher photon energies (Fig. 3). Assuming this mode to be the same one that causes δ_1 , the coupling to this low energy mode is stronger in the upper state of the electronic transition than in the ground state. We

shall comment further on this subject in Section IV below.

In the same temperature range beginning at about 6 K, we observe anti-Stokes replicas for the phonon modes L_1 - L_3 as shown in detail in Fig. 3. The observed distances from the electronic line in this case are 4.7 ± 0.1 meV for the L_1 anti-Stokes replica (called L_1^A in Table II), and 6.4 ± 0.2 meV for L_2^A . A similar peak corresponding to L_3^A can be observed, about 8.1 meV above L_0 . It is difficult to establish this value since L_3^A is broader than L_1^A and L_2^A (as is also the case for L_3 compared to L_1 and L_2 on the Stokes emission side). These observations directly confirm that the features L_1 - L_3 are phonon replicas, and not electronic transitions. Apparently these discrete phonons are of somewhat smaller energy in the upper electronic state of the optical transition (Table II). This is in agreement with the data from PLE spectra [15]. An important observation in connection with the observed anti-Stokes replicas in Fig. 3 is the unusually high strength of these transitions at a very modest temperature rise. Anti-Stokes replicas are observable already at a sample temperature of 6 K, which is not expected in thermal equilibrium according to Bose-Einstein statistics. Even for the lowest energy mode (2.6 meV) no anti-Stokes replica would be expected at 6 K [25]. The occupancy of these discrete vibrational levels for the quasilocalized modes in the upper vibronic state of the COL centre seems to be locally above the level expected from the lattice temperature, at least for the lowest excited vibrational state.

III:3 Temperature quenching of the COL emission

In addition to the appearance of discrete anti-Stokes phonon replicas in the spectrum, the variation of emission intensity with temperature gives other information about the electronic and vibrational properties of the centre. In the low-temperature region 2-45 K, the relatively strong phonon

coupling dramatically influences the electronic line. (This line, of course, is not strictly a pure electronic line, rather it is a broadened quasi-line with the average value of emitted and absorbed lattice phonons equal to zero. We shall refer to this line as the electronic, or zero-phonon line, though.) Already at the very lowest temperatures the line has a finite width, exceeding its radiative width. This is caused by various broadening mechanisms, including interaction with very small phonons in the acoustic band on the low energy side [25]. The integrated area under the zero-phonon quasiline as well as its peak intensity remains constant at the lowest temperatures ($T < 10$ K). At higher temperatures the electronic line is thermally broadened as theoretically described by non-linear coupling terms in the adiabatic potential [18,25].

The integrated intensity is gradually quenched as the temperature is raised and finally the line totally disappears at a temperature of about 45 K. At the same time all discrete replicas associated with the zero-phonon line also vanish, and left is just the broad featureless emission envelope, which is now broadened at the high energy side, extending well above the position of the electronic transition (Fig. 4). This quenching behaviour of the electronic line is a consequence of electron-phonon coupling already in the linear approximation [25]. It does not affect the integrated intensity of the total emission very much, in agreement with the simple theory for linear electron-phonon coupling to a phonon continuum which predicts a constant total intensity [25]. A more detailed quantitative discussion of this temperature quenching of the electronic line is given below under Section IV.

If the temperature is raised further, electronic quenching processes will be important, and render the whole emission undetectable above 140 K. The behaviour is different for extrinsic and intrinsic excitation, as shown in Fig. 5. With extrinsic excitation no significant quenching occurs

until above 100 K, where a rapid decrease corresponding to an activation energy of 153 ± 5 meV is observed. On the contrary a slight increase of intensity is noted in the temperature interval above 20 K until the quenching process becomes dominating. For intrinsic excitation the final step is similar, but here a gradual decrease occurs so that the total quenching can be described by an expression

$$\frac{I(T)}{I(0)} = \frac{1}{1 + C_1 e^{-E_1/kT} + C_2 e^{-E_2/kT}} \quad (1)$$

with $C_1 = 10$, $E_1 = 11 \pm 1$ meV, $C_2 = 6 \cdot 10^9$, $E_2 = 153 \pm 5$ meV. The fit to the experimental values is shown in Fig. 6.

Care should always be taken when interpreting quenching measurements taken with bandgap excitation. In the case of the GaP:N luminescence, for example [26], equilibrium is not established below 100 K between bound excitons, free excitons and free particles. Reliable quenching data are then obtained only with selective excitation. In our case the significant difference between extrinsic and intrinsic excitation for temperatures up to about 100 K might therefore be expected. What is surprising, however, is the sudden rise of the intensity in the former case just before the rapid quenching starts. This behaviour is possibly due to increased two step excitation over shallow donors, which are emptied thermally in this temperature interval. In the case of bandgap excitation, on the other hand, the small activation energy of 11 meV cannot be assigned to the particles of the bound exciton, which are assumed to have comparable binding energies [15]. The observed decrease of the total intensity might in fact be related to the above mentioned nonequilibrium effects [26], and not to any electronic or vibrational properties of the COL centre.

The larger activation energy 153 meV is similar for both types

of excitation. Using the recently revised value of 2.35 eV for the bandgap energy [27] the total binding energy for the exciton complex will be about 170 meV. Taking an average value of 20 meV for the free exciton binding energy, the difference is 150 meV. This energy therefore corresponds to the thermal release of the exciton as a whole, what might be expected if both particles have comparable binding energies. This has been observed previously, e.g. for excitons bound to NN pairs [26], in contrast to the cases where the most loosely bound particle is thermally released first [28].

IV. Analysis of the shape of the optical emission spectrum

IV.1. Formalism for low temperature spectra

When analysing an experimental spectrum, several different types of vibrations usually must be considered. In the adiabatic and Condon approximations, assuming harmonic vibrations in the crystal, we have a simple model in which the purely electronic line is described by a δ -function. This line is accompanied by a sideband from interactions between the electronic transition and the vibrational modes of the crystal. The sideband can have sharp structure, of finite width though, e.g. resulting from interactions with band vibrations close to the limiting frequencies of the Brillouin zone boundaries [25]. If there are localized vibrations at the defect, the spectrum contains discrete peaks in addition to this continuous spectrum [20,22,25]. These impurity-induced vibrational modes are sharp with rapid space attenuation of the vibrational amplitude. The modes of frequency above the maximum frequency of the band phonons are called true local modes, but gap modes if they fall into the frequency gap between the acoustic and optical phonon branches of the host crystal.

Quite sharp peaks may also occur superimposed on the continuous spectrum, similar to the contributions from the localized vibrations. Such modes, which are resonant with the continuum phonon spectrum, are usually referred to as "quasilocalized" or in-band resonance vibrations [22,25]. These modes are localized in frequency but not in space, and their width increases with the density of lattice modes. Thus sharp quasilocalized modes may be introduced by the impurity into regions of the frequency spectrum, which normally contain low density of states. Localized vibrations and quasilocalized ones make identical contributions to the spectrum, as far as e.g. temperature dependence is concerned [25].

In the absence of true local modes in the COL spectrum, we first focus on the interaction with one particular quasilocalized mode. The spectrum then consists of a basic shape repeated at equidistant energies $n \hbar \Omega_\lambda$ ($n = 1, 2, 3, \dots$), provided that the studied discrete mode (of energy $\hbar \Omega_\lambda$) is independent of other modes in the spectrum. The basic shape, being the electronic line and its vibrational sidebands, includes the continuous band modes and high density peaks at the zone boundaries. This has been referred to as a similarity law of the vibrational wings [25] and is equally valid for the case of true local modes.

The probability for a transition between two electronic states can now be written for the s -th replica of the basic shape ($kT \ll \hbar \Omega_\lambda$) [25]:

$$W(0 \rightarrow s) = W_{0s} \left\langle \prod_{\delta} W_{\delta} \right\rangle_T = W_{0s} I_{\delta}(\omega, T) \quad (2)$$

Here $W_{0s} = \exp(-p_\lambda) p_\lambda^s / s!$ is the Franck-Condon integral, a weight factor by which the s -th replica of the basic shape, $I_{\delta}(\omega, T)$, is multiplied (p_λ is the dimensionless Stokes loss [25]). $\left\langle \prod_{\delta} W_{\delta} \right\rangle_T$ is the transition probability in the system of low energy band vibrations averaged over the initial vibrational states in thermal equilibrium, if the temperature is

too low for any discrete impurity-related modes to be excited. This factor is the basic shape of the spectrum.

At higher temperatures the factor W_{0s} has to be replaced by a thermal average over the initial vibronic state in the optical transition. In reality the electronic line has a finite width and consequently all its replicas. Still this simple basic approximation is found to hold in many cases, especially in systems with a moderate phonon coupling, where a narrow electronic transition occurs at low temperatures in strain-free crystals.

A generalization to the case of many independent discrete defect-related modes is straightforward. As before we assume the adiabatic, Condon and harmonic approximations, and that no changes take place in the inter-atomic force constants during the electronic transition. With L such modes of frequencies $\Omega_1, \Omega_2, \dots, \Omega_L$ the probability distribution function is the sum of the basic shape $I_\delta(\omega, T)$ and its replicas shifted by distances given by the sums and differences of these frequencies. At temperatures too low to excite any of these localized modes only the sums need to be considered, while the anti-Stokes contributions are negligible.

In the case of emission at low temperatures the probability distribution is given by

$$I(\omega, T) = \sum_{\{s_\lambda\}} I_\delta(\omega - \sum_\lambda s_\lambda \Omega_\lambda; T) \cdot \prod_{\{s_\lambda\}} W_{0s_\lambda}(\lambda) \quad (3)$$

where $I_\delta(\omega, T)$ is the basic shape of the electronic line and its associated phonon wing from the coupling to the continuous phonon bands [25]. The sum includes all possible sets $\{s_\lambda\}$ of changes in the discrete vibrational states, where s refers to the number of phonons emitted by the mode λ . The integrated intensities of the quasilines, which are replicas of the zero-phonon line are (at $T=0$)

$$S_0^{s_\lambda}(T) = \exp \left(- \sum_{\delta} p_{\delta} \right) \prod_{\{s_\lambda\}} W_{0s_\lambda}(\lambda) = e^{-S} \prod_{\{s_\lambda\}} e^{-p_\lambda \frac{p_\lambda^{s_\lambda}}{s_\lambda!}} \quad (4)$$

Here $S = \sum_{\delta} p_{\delta}$ is the Huang-Rhys factor characterizing the coupling to the continuum phonon spectrum. The factor $\exp(-S)$ is the relative intensity of the zero-phonon line to the total emission intensity, in the absence of discrete modes. From eq. (4) we see that the relative integrated intensity of the zero-phonon line compared to the total emission equals

$$S_0^0(T=0) = e^{-S} \exp \left(- \sum_{\lambda=1}^L p_{\lambda} \right) = \exp(-S) \exp(-S_{\lambda})$$

where S_{λ} denotes the contribution of the discrete quasilocalized modes to the coupling. For each mode in the set $\{s_{\lambda}\}$ the coupling constant p_{λ} is deduced from the ratio of the first replica and the zero-phonon line. This is realized from eq. (4) by setting one of the modes, say λ' , in the set $\{s_{\lambda}\}$ to 1 and the rest to zero. This gives

$$\frac{S_0^{s_{\lambda'}=1}(T=0)}{S_0^0(T=0)} = \frac{e^{-S} \cdot \exp \left(- \sum_{\lambda=1}^L p_{\lambda} \right) \cdot p_{\lambda'}}{e^{-S} e^{-S_{\lambda}}} = p_{\lambda'} \quad (5)$$

IV:2. Analysis of phonon replicas in the COL spectrum

Low temperatures

Comparing the phonon energies present in the COL spectrum (Fig. 1 and Table 1) with the phonon dispersion curves of GaP (Fig. 7) [29], we see that no true local modes are seen in the emission spectrum of the COL. However, a number of discrete modes resonant with the acoustic phonon branches, or lying in the forbidden phonon band gap are seen together with the optical phonon replicas. We assign all these modes to discrete

quasilocalized vibrations (except LO_T and TO_T) and the equations given above should describe this spectrum adequately [25].

The Huang-Rhys factor of the COL emission, describing the relative strength of the zero-phonon line and the phonon wings, including both discrete and continuous phonon modes, is given by the ratio between the integrated intensity of the zero-phonon line and the total intensity of the emission. Measured from Fig. 1 this ratio is about 1:150 giving $S_{\text{tot}} = S + S_\lambda = 5$. The quasilocalized modes contribute the sum of their coupling constants to this factor. From Table I where the major discrete modes are listed we have $S_\lambda = \sum_i p_{\lambda i} = 1.5 - 2.0$, depending on which replicas are interpreted as first replicas of single modes only.

The remaining factor $S \approx 3$ illustrates the rather strong coupling to the continuous vibrational bands, mainly the acoustic ones. This is an indication of the importance of deformation-potential coupling at the impurity site in the electron-phonon interaction in optical transitions via this centre [30,31]. The total Franck-Condon (FC) shift of this emission is 65 meV, the position of the maximum of the phonon envelope being displaced that much below the zero-phonon line. Judging the contribution of the discrete phonon modes to the total FC shift we obtain $\Delta FC_\lambda = \sum_\lambda \hbar \omega_\lambda \cdot p_\lambda = 34$ meV, about half of this caused by the LO_T phonon. Coupling to the continuum then causes a Franck-Condon shift of roughly 30 meV with an overall coupling of $S = 3$. This corresponds to an average phonon energy of 10 meV, well consistent with the acoustic phonon branches.

Elevated temperatures

The equations given above all refer to lower temperatures than needed to excite any of the quasilocalized modes present in the spectrum. When the temperature is raised, thermal averages must be taken over all vibrational

states in the excited vibronic state. This is taken care of, if the Huang-Rhys factor is written $S = \sum_j p_j (2\bar{n}_j + 1)$, where $\bar{n}(\omega) = (e^{\hbar\omega/kT} - 1)^{-1}$, is the average occupation number of a vibrational state in thermal equilibrium. The procedure is similar for both continuous and discrete modes. In the latter case the absorption of phonons can be seen as discrete peaks on the anti-Stokes wing, if the coupling is sufficiently strong. This is the case for the three low energy modes of our spectrum as mentioned above. Also the low energy mode of 2.6 meV is activated by thermal occupation of the excited state, the unexpected feature being that it is not detectable in the ground state.

As already mentioned above, the coupling of low energy phonon modes to the electronic line is rather complicated, consistent with the unusual identity of the centre [15]. It seems reasonable to assume that a low energy mode of 2.6 meV couples to both the electronic line and the Stokes replica L_1 , more strongly to the latter. This is found to occur only on the anti-Stokes wing at elevated temperatures (Fig. 3), requiring a stronger coupling to this low energy mode in the excited electronic state. Alternatively it has been suggested that L_2 and L_3 are Stokes replicas of L_1 with that very same mode in the electronic ground state, with reference to the increasing linewidth of these compared with L_1 [3]. This is not a very attractive explanation since it would require a strongly nonlinear coupling to explain the increasing energy difference between L_1 and L_2 (1.5 meV) and between L_2 and L_3 (2 meV). This difference is even greater in the excited state as is clear from PLE measurements [15]. Secondly, a considerable increase in the phonon energy of the excited state when comparing δ_1 - L_1 (2.6 meV) with L_1 - L_2 (1.5 meV) is not in agreement with the observed anti-Stokes measurements and values from PLE measurements. These always show a decrease in phonon energies for the excited state. (For details see Table II).

The most natural assumption is that the modes L_1 - L_3 are in fact three different in-band resonance modes, with linewidths proportional to the increasing density of phonon states in the GaP lattice. The peaks L_2 and especially L_3 are therefore lifetime-broadened more than L_1 . This is in good agreement with observations of three discrete replicas on the anti-Stokes wing, with similar broadening behaviour. At elevated temperatures L_1 decreases at the same time as the double peak $\delta_1 + \delta_2$ increases. Since we interpret this behaviour as a dominant secondary coupling to a mode of 2.6 meV in the case of L_1 and to a 4.6 meV mode in the case of L_2 , the thermal occupation in the excited vibronic state accounts for the more rapid decrease of L_1 . In absorption (PLE), however, the relative strength of the phonon modes B_1 - B_3 is slightly different from that of L_1 - L_3 in emission (with reservation for background effects) [15]. This does not provide any evidence against the idea of these modes being three independent ones, particularly since their energies agree with the anti-Stokes components within experimental accuracy (Table II). The observed intensity differences of B_1 - B_3 compared with L_1 - L_3 are most naturally explained in terms of the action of a low energy mode coupling to B_1 , which could unfortunately not be resolved in the background in PLE data.

The possible assignments for these various discrete quasilocalized modes depend on the assumptions made for the defect geometry. The g-values for the 2.1774 eV transition is nearly isotropic, and Zeeman measurements give therefore only very limited information about the orientation of the defect axis. Also the higher resolution of ODMR is not applicable in this case, due to strong thermalization of the initial triplet state. Therefore, so far the defect symmetry has not been deduced from the optical measurements [15].

Two different interstitial sites exist in the zincblende lattice, the hexagonal and the tetrahedral interstitial sites [32]. Without knowledge

about the defect symmetry both a linear $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ defect and a non-linear one have to be considered. In the linear defect the Cu_I atoms occupy tetrahedral sites, whereas a bent $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ defect results if both Cu_I atoms are on hexagonal sites.

A linear defect with three atoms is expected to possess inversion symmetry and by analogy with molecular theory four independent normal modes of vibration exist. Of these, only one is even under interchange of the equivalent Cu_I atoms and thus allowed in the adiabatic model. Considering only the vibrational degrees of freedom connected with the two unbonded Cu_I atoms the symmetric mode of vibration along the defect axis is still even under inversion. Therefore the normal modes of a linear defect are not obviously consistent with the quasilocalized modes observed in the spectrum.

A perfectly linear $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ defect might not be the most natural configuration for the COL defect. Although the linear defect is more easily formed for electrostatical reasons, the interstitials may prefer the hexagonal sites by strain symmetry, with a bent configuration as a result. Three normal modes are expected from the theory of molecular vibrations for a bent defect of low symmetry (C_{2v}) [33]. Two of these have even parity under reflections in the plane bisecting the defect angle. These replicas could cause the L_1 and L_2 modes, if the L_3 mode corresponds to the odd parity mode coupling to L_1 , provided that the allowed and forbidden modes become mixed [16].

The interstitials occupying the essentially nonbonding sites have additional degrees of freedom compared with Cu_{Ga} . It may be more realistic to consider only the six degrees of freedom connected with the two Cu_I atoms. These can be combined to yield three even modes and three odd modes, classified according to parity under reflections which interchange the Cu_I . In the adiabatic model one would expect the even modes to correspond to

L_1 , L_2 and L_3 . Then these are three independent modes as assumed above. This interpretation is apparently a plausible choice, considering only the mode structure. An increased relaxation of the Cu_{Ga} atom might also result from such a bent configuration compared with a linear one, and cause the rather strong phonon coupling observed for the COL centre.

IV:3 Temperature dependence of the zero-phonon line

Formalism

As previously mentioned in Sec. III:3, the integrated intensity of the zero-phonon quasiline rapidly decreases with increasing temperature and disappears at a rather low temperature, about 45 K (Fig. 4). The total intensity of the phonon sidebands, however, retains most of the strength up to about 70 K, whereafter it decreases fast, to finally disappear at 140 K (Fig. 5). The most obvious change at lower temperatures is therefore the gradual disappearance of the fine structure together with the zero-phonon line as the temperature is raised. Such behaviour is commonly observed in the spectra of colour centres, e.g. for the N_1 band of NaCl [20] as well as for internal transitions within 3d-ions in solids [34]. The intensity of the zero-phonon transition decreases as transitions involving thermally stimulated emission or absorption of phonons become more probable. Absorption of a phonon from the warm lattice contributes a sideband on the high energy side of the line in emission with a strength proportional to $\bar{n}(\omega) = [e^{\hbar\omega/kT} - 1]^{-1}$. Stimulated emission of a phonon into the warm lattice increases the strength of the low energy sideband proportional to the factor $[1 + \bar{n}(\omega)]$. Both these processes compete with the zero-phonon transition and cause the decrease in its strength together with broadening of the multiphonon band. In the adiabatic, Condon and harmonic approximations (as above) the zeroth moment of the transition

probability gives the integrated intensity of the zero-phonon line in the case of linear coupling [25].

$$S_0^0(T) = \exp \left[- \sum_{\lambda=1}^L p_{\lambda} (2\bar{n}_{\lambda} + 1) \right] \cdot \prod_{\lambda} I_0 \left(p_{\lambda} \left[\sinh \left(\frac{\hbar \omega_{\lambda}}{2kT} \right) \right]^{-1} \right) \cdot \exp \left[- \sum_{\delta} p_{\delta} (2\bar{n}_{\delta} + 1) \right] \quad (6)$$

I_0 is the zeroth Bessel function which is close to unity at low temperatures. The label λ refers to the L local or quasilocalized modes described by the equation. Other notations are the usual ones. Apart from the Bessel function which can be ignored in the temperature interval of interest here, the coupling to discrete modes and band phonons is described by identical expressions. The decreasing intensity of the zero-phonon line is expressed through the temperature dependence of the Huang-Rhys factor

$$S_{\text{tot}} = \sum_{\lambda} p_{\lambda} (2\bar{n}_{\lambda} + 1) + \sum_{\delta} p_{\delta} (2\bar{n}_{\delta} + 1)$$

The factor $e^{-S_{\text{tot}}}$ plays the same role as the Debye-Waller factor plays in the theory of the Mössbauer effect [18]. Defining a weighted density of phonon states $\rho(\omega)$ from the energy V which describes the difference between the energies of the crystal before and after the electronic transition

[18], $V = \sum_S V_S A_S + \sum_{S,S'} V_{SS'} A_S A_{S'}$, we have

$$\rho(\omega) = \sum_S V_S^2 \delta(\omega - \omega_S). \quad (7)$$

With the aid of eq. (7) an expression for the Huang-Rhys factor in absence of localized modes is written [18]

$$S(T) = \left(\frac{1}{\hbar^2} \right) \int_0^{\infty} d\omega [\rho(\omega)/\omega^2] [2\bar{n}(\omega) + 1] \quad (8)$$

The phonon density function $\rho(\omega)$ reflects the frequency distribution of the host crystal and in the limit of weak coupling it can be determined from the one phonon spectrum. For $S=0.1$ the shape function of the one

phonon sideband contributes more than 90 % of the total phonon sideband. For a larger coupling constant iterative methods exist for deducing the one phonon sideband and the density function [21,35]. In some cases the Debye approximation is an adequate approximation to describe the low frequency modes of the perturbed crystal [20].

In the case of the COL emission the several discrete quasilocalized modes resonant with the band phonon branches cause complications in the analysis. From the estimate of the discrete coupling constants above, the contribution of the quasilocalized modes to the quenching of the zero-phonon line can be approximated. The low energy mode of 2.6 meV does not appear in the Stokes sideband, and is therefore not included in the estimated coupling strength. This is probably unsatisfactory. Having isolated the discrete modes we can describe the low frequency continuum modes of the crystal with the Debye approximation, giving for the integrated intensity of the zero-phonon line [18,20]

$$I(T) = \exp \left(-S \left[1 + \left(2\pi^2/3 \right) (T/\theta_D)^2 \right] \right) \quad (9)$$

Often the values of θ_D obtained by fitting the experimental data to this expression do not agree with the characteristic Debye temperatures determined from specific heat measurements. This difference may indicate a stronger coupling to the band modes than assumed, or associate the coupling to one specific branch of phonons selectively [20].

Comparison with experimental data for the zero-phonon line

When fitting the theoretical values to the experimental ones several difficulties arise. As shown above the COL centre in GaP has a complicated phonon coupling, in particular it is difficult to evaluate the coupling strength of the phonon mode of 2.6 meV due to anomalous coupling to the

zero-phonon line. Also an estimate of the coupling constants of the discrete modes $(L_1^A - L_3^A)$ on the anti-Stokes wing gives considerably higher values than deduced from the Stokes wing. The strong intensity of these components indicates a raised local temperature at the defect, compared with the measured temperature of the sample. Such discrete "hot bands" are common in molecules [20]. Clearly these quasilocalized modes, which are excited thermally at higher temperatures than the low frequency acoustic modes, are not expected to play an essential role at low temperatures, when kT is far below the energy of these modes. However, due to the possible "hot" behaviour of such modes, we cannot be certain of their role in the quenching of the zero-phonon line.

Judging from the phonon sideband immediately following the zero-phonon line, the low frequency acoustic band modes seem to couple strongly to the line. The phonon envelope can only be approximated with the one-phonon sideband in cases of weak coupling. Therefore an evaluation of the phonon density $\rho(\omega)$ from the emission spectrum implies that integrating procedures have to be employed [35]. If we instead consider the Debye approximation to be sufficiently accurate description of the continuous lattice modes for our purposes, the corresponding temperature dependence is described in eq. (9).

To be able to account for the rapid decrease of the electronic line with rising temperature, however, the important role of the quasilocalized modes has to be included in the evaluation. Eq. (6) combines the separate contributions of discrete and continuous modes. If we insert the Debye approximation for the contribution of continuous modes into eq. (6) the curve in Fig. 8 results. A few comments on the parameters in the equations are needed. The ratio between the zero-phonon line and the total emission gives the Huang-Rhys factor $S=5$. The low temperature value for the Debye temperature of GaP is $\theta_D=300$ [37]. In Table I the coupling constants of the modes $L_1 - L_3$ are given, although the slightly higher values $p_\lambda=0.6$

for L_2 and $p_\lambda = 0.5$ for L_1 and L_2 are needed to describe the temperature dependence. This fact might be related to the strong anti-Stokes components observed for these modes. Also the value $p_\lambda = 0.5$ is chosen for the 2.6 meV mode, since this mode is found to be necessary in the calculation.

The evaluated temperature dependence shows that the major contributions to the quenching of the electronic line come from the discrete modes. A detailed evaluation of the phonon density of states $\rho(\omega)$ and the use of eq. (8) might increase the relative importance of the continuous modes in the estimate, and would certainly be a more satisfactory approach than the Debye approximation. The dominating influence of the discrete quasilocalized modes would, however, hardly be altered in such a model. The procedure presented here therefore clarifies the relevance of phonon coupling as the main cause of the thermal quenching of the electronic line in the COL emission and the relative importance of different types of phonon modes.

V. Conclusions

In this paper we present important complementary information to the previous knowledge about the properties of the COL-centre in GaP. There was a great interest in this centre about 10 years ago, since it was then believed to be a $V_{\text{Ga}}-O_p$ complex, and in addition an important prestage in the formation of some other radiative isoelectronic centres such as Zn-O, Cd-O, or Li-Li-O in GaP [8-10, 22]. Later it was realized that the COL centre involves only Cu [3], and it is now identified as an isoelectronic $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ complex [15].

The phonon coupling associated with the electronic transition is unusual and characteristic for the COL bound exciton. A rather strong coupling to continuum modes as well as to several quasilocalized modes is

present. These modes have also been observed in absorption [15]. Measurements at low temperatures and elevated temperatures reveal a quite complex coupling to low energy discrete modes. A phonon mode of 2.6 meV is found to interact with the electronic line only in the excited vibronic state, and this mode is even found to couple in a similar way to the first discrete quasilocalized replica. Effects of nonlinear coupling are seen in the reduction of phonon energies on the anti-Stokes wing, in agreement with observations in absorption spectra.

The strong coupling to low energy phonons manifests itself in the thermal quenching of the electronic line already at 45 K. A theoretical evaluation estimates qualitatively the roles of the low energy continuum modes and the discrete quasilocalized modes in this quenching. The total emission intensity remains largely unaltered as a smooth emission band up to about 80 K, until dissociation of the electronic particles from the complex becomes important. A thermal activation energy equal to the binding energy of the COL bound exciton is deduced. Therefore a thermal release of the exciton as an entity is concluded, in agreement with the assumption of both particles being tightly bound [15].

A detailed theoretical evaluation of the relation between the unusual discrete phonon modes characteristic for the COL and the degrees of freedom of the Cu_I atom in the $\text{Cu}_I\text{-Cu}_{\text{Ga}}\text{-Cu}_I$ complex is unwarranted at the moment, since neither ODMR nor Zeeman measurements reveal the symmetry axis of the defect.

References

1. D.R. Wight, J.W.A. Trussler and W. Harding, Proc. XIth Conf. on Semiconductors (Warsaw, 1972) p. 1091.
2. E. Fabre and R.N. Bhargava, Appl. Phys. Lett. 24, 322 (1974).
3. P.J. Dean, J. Luminescence 7, 51 (1973).
4. B. Monemar, J. Luminescence 5, 472 (1972).
5. B. Wessels, J. Appl. Phys. 47, 1131 (1976).
6. P.O. Fagerström, H.G. Grimmeiss and H. Titze, J. Appl. Phys. 49, 3341 (1978).
7. H.G. Grimmeiss, B. Monemar and L. Samuelson, Solid State Electron. 21, 1505 (1978).
8. R.N. Bhargava, S.K. Kurtz, A.T. Vink and R.C. Peters, Phys. Rev. Lett. 27, 183 (1971).
9. G.M. Blom and R.N. Bhargava, J. Crystal Growth 17, 38 (1972).
10. P.J. Dean, Solid State Commun. 9, 2211 (1971).
11. B. Monemar, J. Luminescence 5, 239 (1972).
12. P.J. Dean and D.C. Herbert in Topics in Current Physics, Vol. 14, edited by K. Cho (Springer Verlag, 1979) p. 55.
13. B. Monemar in Treatise on Materials, Science and Technology, Vol. 19A (1981) p. 151.
14. B.C. Cavenett, Advances in Physics (1981), to be published.
15. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, unpublished.
16. P.J. Dean, B. Monemar, H.P. Gislason and D.C. Herbert, Proceedings of the ICL Conference (Berlin, 1981).
17. H.P. Gislason, B. Monemar, P.J. Dean and D.C. Herbert, unpublished.
18. A.A. Maradudin in Solid State Physics, Vol. 18, edited by F. Seitz and D. Turnbull (Academic, New York 1966) p. 273.

19. M.H.L. Pryce in Phonons in Perfect Lattice and in Lattices with Crystal Imperfections, Scottish University Summer School in Physics 1965, edited by R.W.N. Stevansson (Oliver and Boyd, 1965) p. 403.
20. D.B. Fitchen in Physics of Color Centers, edited by W. Beall Fowler (Academic, New York, 1968) p. 293.
21. M. Mostoller, B.N. Ganguly and R.F. Wood, Phys. Rev. B4, 2015 (1971).
22. P.J. Dean, Phys. Rev. B4, 2596 (1971).
23. C.H. Henry, P.J. Dean and J.D. Cuthbert, Phys. Rev. 166, 754 (1968).
24. J.L. Yarnell, J.L. Warren, R.G. Wenzel and P.J. Dean, Neutron Inelastic Scattering 1, 301 (Vienna, 1968).
25. K.K. Rebane, Impurity Spectra of Solids (Plenum Press, New York, 1970).
26. M.D. Sturge, E. Cohen and K.F. Rodgers, Phys. Rev. B15, 3169 (1977).
27. B. Monemar and L. Samuelson, Solid State Commun. 26, 165 (1978).
28. J.J. Hopfield, D.G. Thomas and R.T. Lynch, Phys. Rev. Lett. 17, 312 (1966).
29. A.E. Yunovich, Fortschritte der Physik 23, 317 (1975).
30. A.M. Stoneham, J. Phys. C: Solid St. Phys. 12, 891 (1979).
31. Y. Toyozawa, J. Luminescence 1 (2), 732 (1970).
32. J.W. Corbett and J.C. Bourgoin in Point Defects in Solids, Vol. 2, edited by J.H. Crawford, Jr. and L.M. Slifkin (Plenum Press, New York, 1975) Ch. 1.
33. M. Tinkham, Group Theory and Quantum Mechanics (McGraw-Hill, 1964).
34. A.P. Radlinski, J. Phys. C: Solid St. Phys. 13, 2407 (1980).
35. M.N. Sapozhnikov, phys. stat. solidi (b) 75, 11 (1976).
36. N.N. Sirota in Semiconductors and Semimetals, Vol. 4, edited by R.K. Willardson and A.C. Beer (Academic Press, New York, 1968).
37. R.M. Hoff and J.C. Irwin, Can. J. Phys. 51, 63 (1973).

Table I

Notation	Relative intensity (%)	Photon energy (eV)	Energy shift (meV)	Interpretation
L_0	100	2.177	0	Zero-phonon line
L_1	21	2.172	5.3 ± 0.1	
L_2	28	2.170	6.8 ± 0.1	
L_3	21	2.169	8.8 ± 0.1	
L_4	2	2.165	12.0 ± 0.2	$(L_1 + L_2)$
L_5	2	2.164	13.5 ± 0.2	$(L_2 + L_2)$
L_6	1	2.163	14.3 ± 0.3	$(L_1 + L_3)$
L_7	14	2.159	18.1 ± 0.5	TA
L_8	37	2.150	27.1 ± 0.2	LA (distorted)
L_9	2	2.145	32.5 ± 0.3	LA + L_1
L_{10}	7	2.144	33.7 ± 0.3	LA + L_2
L_{11}	6	2.142	35.6 ± 0.3	LA + L_3
L_{12}	3	2.138	39.7 ± 0.3	
L_{13}	2	2.132	45.4 ± 0.3	TO_{Γ}
L_{14}	29	2.127	50.1 ± 0.3	LO_{Γ}
L_{15}	7	2.122	55.0 ± 0.7	2 LA
L_{16}	7	2.100	77 ± 1	

Table II

Emission				Absorption (PLE) ³⁾	
Stokes		Anti-Stokes			
Replica	Energy, meV ¹⁾	Replica	Energy, meV ¹⁾	Replica	Energy, meV ²⁾
L ₁	5.3 (1.5) ⁴⁾	L ₁ ^A	4.7 (1.7)	B ₁	4.5
L ₂	6.8 (2.0)	L ₂ ^A	6.4 (1.7)	B ₂	6.0
L ₃	8.8	L ₃ ^A	8.1	B ₃	8.7
		$\partial_1 - L_1$	2.6		
		$\partial_2 - L_2$	4.6		

1) Accurate to ± 0.1 meV

2) Accurate to ± 0.2 meV

3) Values from Ref. [15]

4) Energy difference between adjacent replicas is shown in parentheses

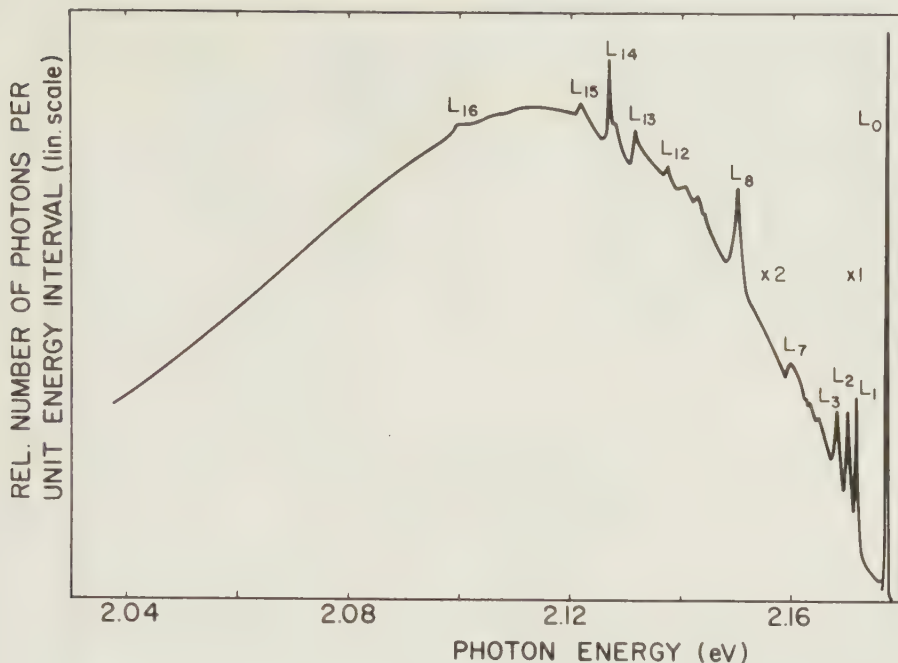


Fig. 1(a) Photoluminescence spectrum of the COL emission measured at 2 K for a Cu-doped GaP epitaxial layer, excited with a 5145 Å Ar⁺-laser line. The zero-phonon line (L_0) occurs at 2.1774 eV. Energies of the phonon replicas labelled L_1 - L_{16} are listed in Table I.

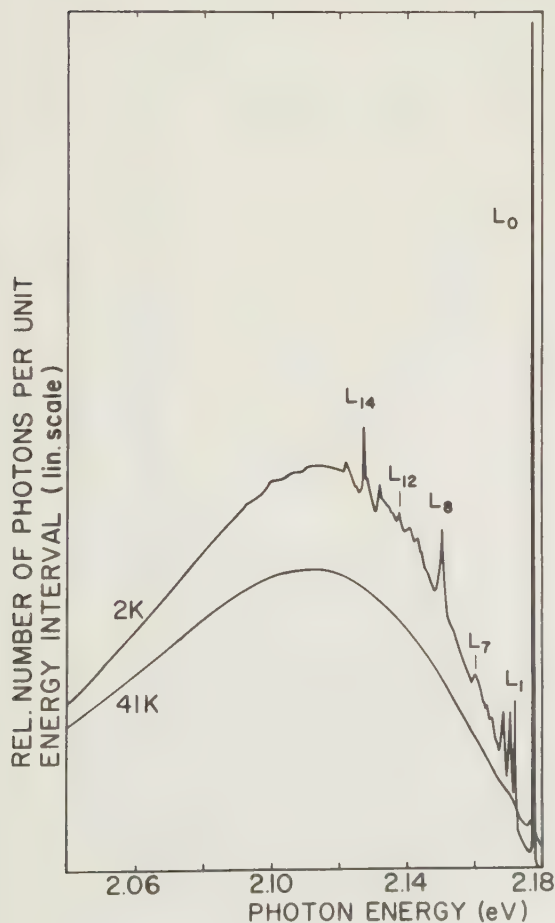


Fig. 1(b) The same spectrum as in (a). A spectrum measured at 45 K is also included. At this temperature the electronic line and the discrete structure have vanished. A slight decrease is noted in the total emission intensity.

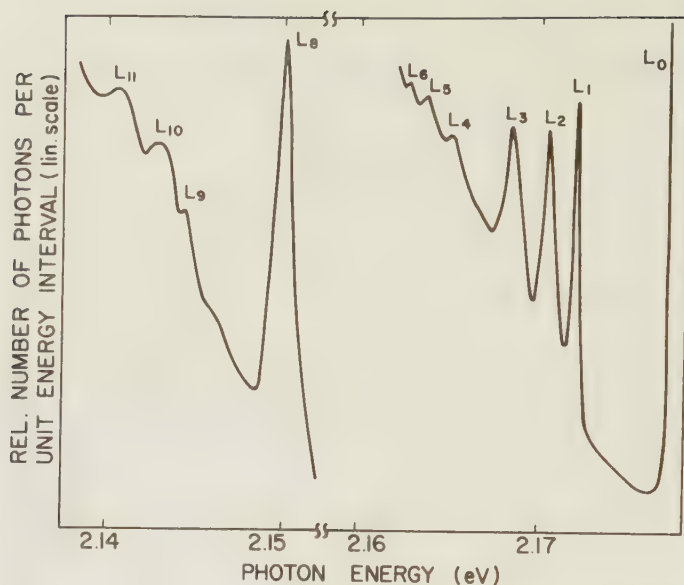


Fig. 2 Selected parts of the photoluminescence spectrum in Fig. 1, on an expanded energy scale to show more clearly the discrete low energy phonon replicas associated with the zero-phonon line and the strong L_8 replica. For phonon energies see Table I.

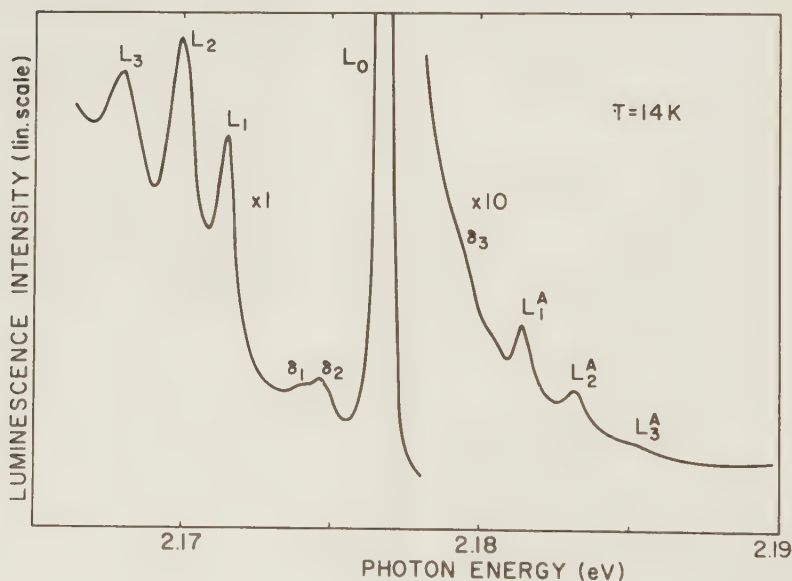


Fig. 3 Selected part of the photoluminescence spectrum at 14 K for the same crystal as in Fig. 1 and Fig. 2. The spectrum shows two new peaks δ_1 and δ_2 between the zero-phonon line L_0 and L_1 , which were not present at the lowest temperatures. At this temperature the anti-Stokes replicas δ_3 and $L_1^A - L_3^A$ are also clearly observed. For phonon energies and comparison with PLE measurements see Table II.

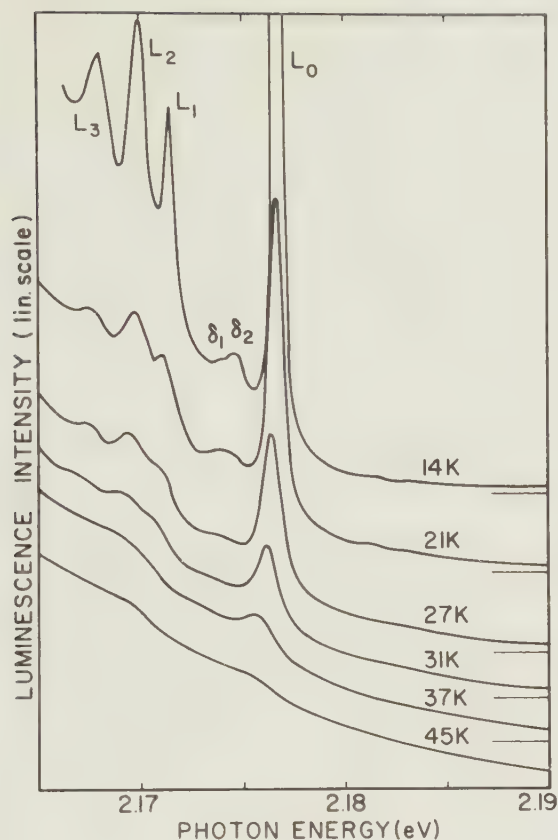
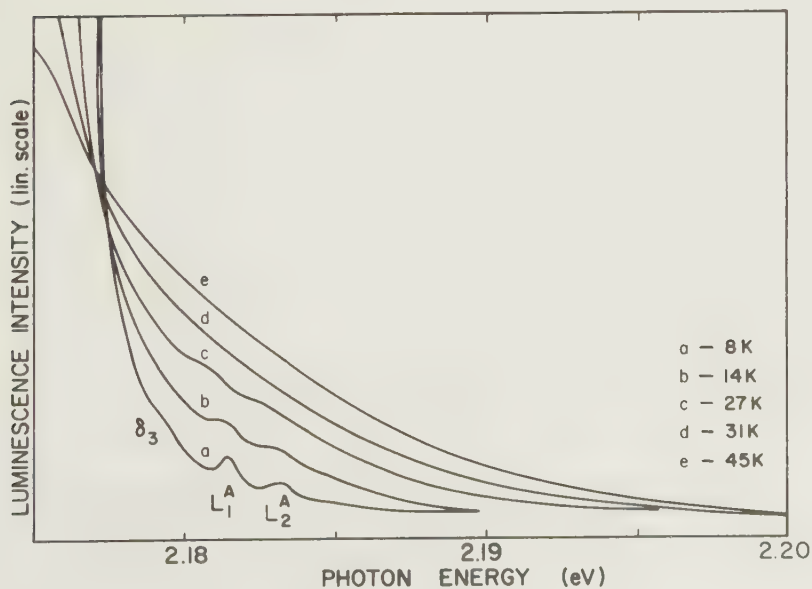


Fig. 4(a) Portion of the COL emission showing the zero-phonon line and its low energy phonon replicas at different temperatures from 14 K to 45 K. The broadening and temperature quenching of the zero-phonon line and its discrete Stokes replicas are clearly shown.

Fig. 4(b) Detailed behaviour of the anti-Stokes region of the spectra in (a), at temperatures from 8 K to 45 K. Note that the integrated strength of the anti-Stokes region increases at the same time as the zero-phonon line decreases in intensity as expected from theory.



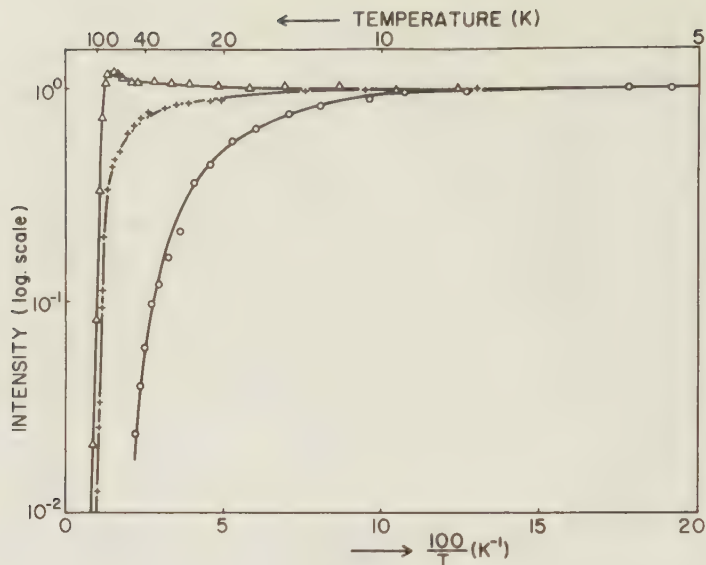


Fig. 5 Temperature dependence of the COL emission. Experimental points (Δ) denote the integrated intensity of the total emission measured with extrinsic excitation (≈ 5500 Å), while (+) denotes the same quantity measured with intrinsic excitation (5145 Å). Also shown (O) is the temperature dependence of the zero-phonon line, taken with intrinsic excitation (5145 Å). In this case no difference in the thermal quenching behaviour was seen for intrinsic and extrinsic excitation.

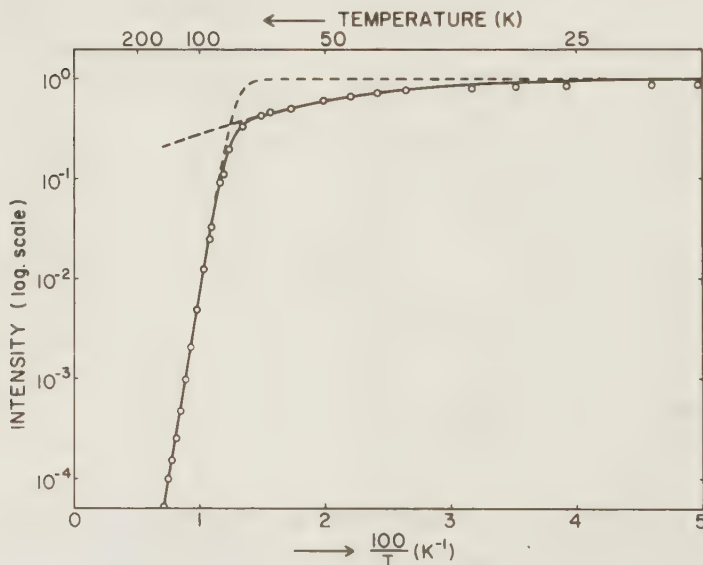


Fig. 6 Illustration of the fit of eq. (1) to the thermal quenching behaviour of the total emission intensity with intrinsic excitation (curve (+) in Fig. 5). The separate contributions of the two exponentials in eq. (1) are also shown (---).

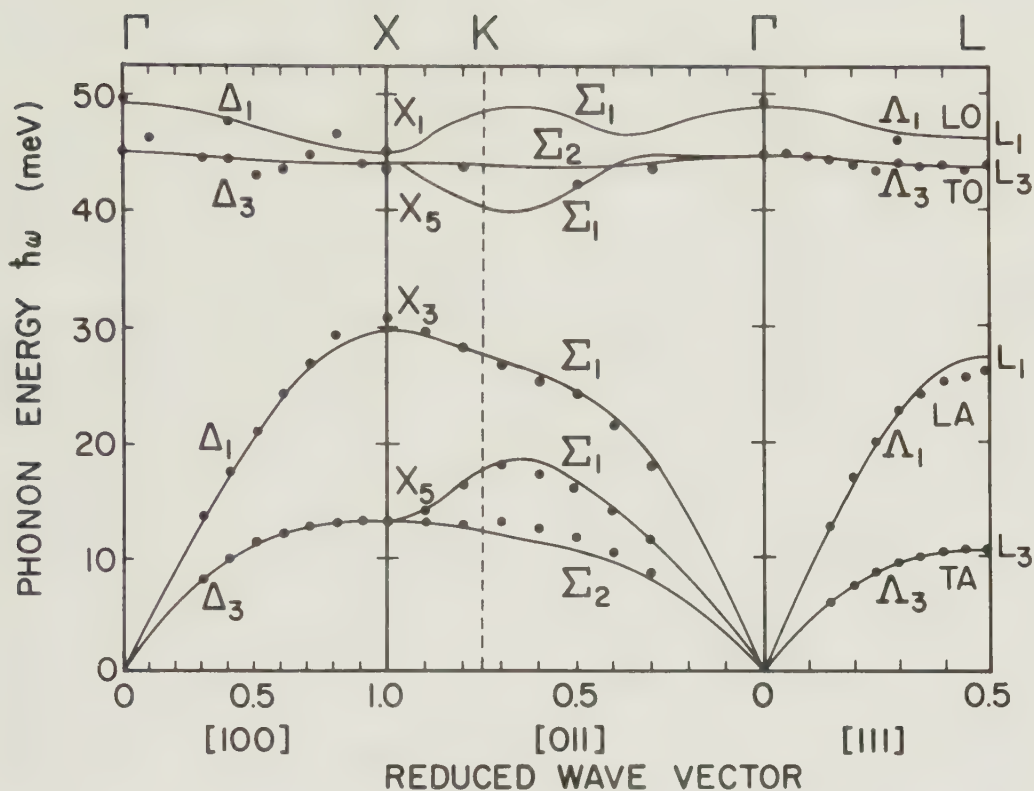


Fig. 7 Dispersion curves for the phonon spectrum of GaP, measured at 300 K [24]. The solid lines represent a shell-model fit to the data. The branches are labelled with the irreducible representations, according to which the associated polarization vectors transform. A point defect can introduce different types of vibration modes into the phonon spectrum of the crystal. Localized modes have frequencies above the maximum frequency of the unperturbed host crystal (true local modes), or in the gap between the optical and acoustic branches of the frequency spectrum (gap modes). A third kind of impurity induced modes are the resonance modes. These are localized in frequency but not in space and occur at frequencies resonant with the phonon bands of the crystal (quasilocalized - or in-band resonance modes).

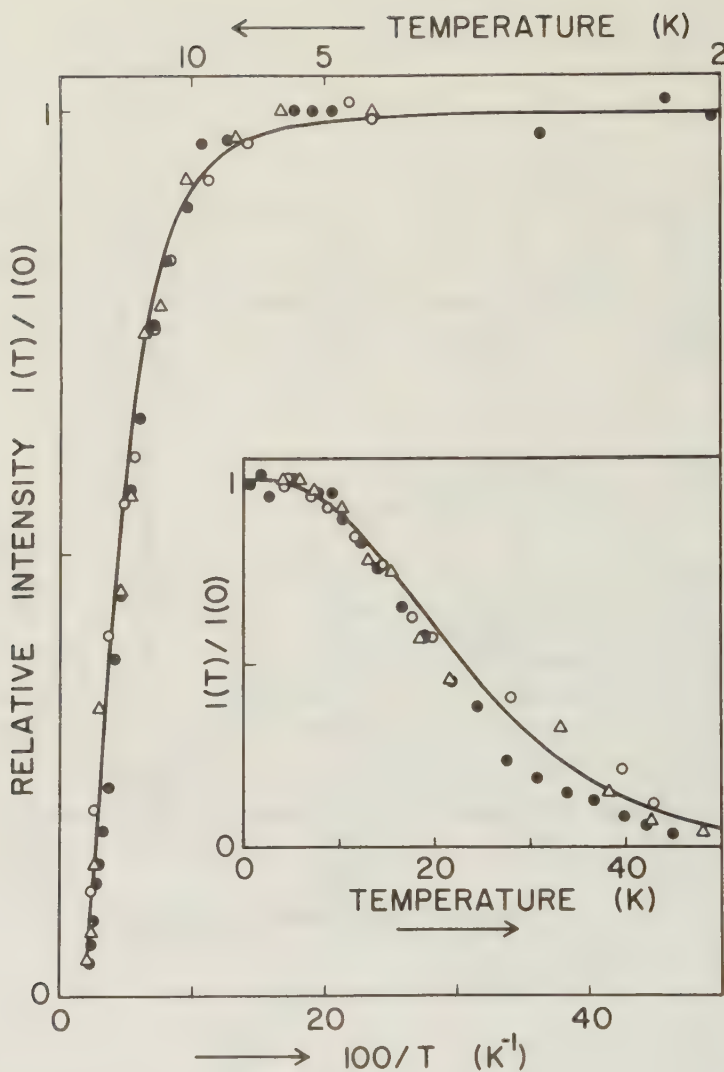


Fig. 8 Linear plot of the temperature quenching of the integrated intensity of the zero-phonon line as a function of $100/T$ and on inset as a function of the temperature T . The experimental values ($\bullet$) are the same as in Fig. 5, measured with intrinsic excitation at 5145 Å. The values (Δ) are also measured with excitation at 5145 Å, while the points ($\circ$) are taken with extrinsic excitation at 5500 Å. The theoretical evaluation is made with the parameters $S=5$ and $\theta_D=300$ in eq. (9), and four quasilocalized phonon modes according to eq. (6). The phonon energies are 2.6 meV, 5.3 meV, 6.8 meV, and 8.8 meV with coupling constants $p_\lambda=0.6$ for the 6.8 meV mode and 0.5 for the other modes.

Neutral defect complexes in GaP doped with Cu and Li.

by

H.P. Gislason and B. Monemar

University of Lund, Department of Solid State Physics

Box 725, S-220 07 LUND, Sweden

and P.J. Dean, RSRE, Gt. Malvern, Worcs. WR14 3PS, England

and S. Depinna and B.C. Cavenett, Department of Physics,

The University, Hull, HU6 7RX, England

Abstract

Four new emissions are observed after Cu- and Li diffusion of GaP, all related to the simultaneous presence of both dopants in the host material. These emissions are studied with photoluminescence techniques, including photoluminescence excitation measurements and magneto-optical work. The corresponding four centers, $(\text{Cu-Li})_{\text{I-IV}}$, bind excitons with localization energies 23 meV (I), 53 meV (II), 87 meV (III) and 213 meV (IV). All emissions contain sharp no-phonon lines and particularly $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{III}}$ show structured phonon sidebands with well resolved replicas. The four groups of BE transitions consist of triplet-singlet pairs, characteristic for the case where the angular orbital momentum of the hole wavefunctions is quenched in an axial field. Upon the addition of an electron the BE states with $J=0$ and 1 are formed. The different spectra exhibit different J-J coupling, $\Delta_{\text{JJ}} = 1$ meV (I), 1.9 meV (II), 2.1 meV (III) and 7 meV (IV), resulting in different relative intensities of the triplets and singlets in the pairs. The extent to which the triplet has pure spin character is also important for the intensity ratio. In addition to a triplet-singlet pair $(\text{Cu-Li})_{\text{III}}$ shows a second singlet, observed at higher temperatures. It is suggested that this state results from a splitting of the electron states corresponding

to the splitting of the $J=3/2$ hole states in local axial strain field. Tentative models are presented for the identities of the four centers. It is argued that all centers are neutral and contain three impurity atoms (Cu or Li). If they occupy one Ga-site and two interstitial sites neutral and spin-free centers are formed. The identification of the centers is based on the relative binding energy connected with hole binding to complexes containing Cu_{Ga} and Li_{Ga} respectively. Also, simple electrostatic arguments for the repulsion upon formation of neutral spin-free centers are considered. Such centers of the molecular isoelectronic type are expected to exhibit the observed electronic structure of the bound excitons studied.

I. Introduction

Identification and properties of defects in semiconductors are problems of great current interest. Such defects are characterized and well understood only in some simple cases such as substitutional point defects [1]. Even in this case great problems still exist in characterizing the so called deep level substitutional defects [1]. Unfortunately the high temperature chemical reactions during growth and cool down after growth (or heat treatment) seem to favour the creation of various complexes of impurity atoms and other point defects, particularly for compound semiconductors [2]. The electronic properties of such complexes are even more difficult to predict. Yet, these defects may be very important as persistent recombination centers in semiconductors, for the reason that they often can capture and bind both kinds of carriers [3].

Perhaps the most successful cases of characterization of defect complexes in semiconductors have been carried out with optical spectroscopy, notably for those centers where bound excitons (BE) can be observed [3]. For the reasons of charge neutrality and Coulomb attraction during defect formation at high temperature the most abundant type of complexes is believed to be the electrically neutral associates, which include the so called iso-electronic defects. The atoms taking part in such complexes are arranged to compensate for all valence electrons of the host lattice sites they occupy, so as to form a neutral substitute. Both an electron and a hole (a bound exciton) may be bound to these centers at low temperature [3]. This type of defects has been studied in some detail in materials such as GaP. Good examples are the Zn-O and Cd-O complexes occupying nearest neighbour sites [4,5], or the so called NN-pairs consisting of two N atoms substituted at P-sites separated by various distances [6]. Electronically these cases are reasonably well understood in terms of the so called Hopfield-Thomas-Lynch model [7]. Here one particle is deeply bound in a localized potential (the

electron in the above mentioned examples) while the second particle is bound in a shallow state by a Coulomb-like potential in the presence of the primary particle [7]. The ground state properties of the bound exciton thereby formed can usually be understood in terms of the expected J-J splitting and internal axial strain field of the defect [3,8].

A more complicated class of complexes arises when interstitial atoms are also involved. A good example of such a case is the $\text{Li}_\text{I}-\text{Li}_{\text{Ga}}-\text{O}_\text{P} \langle 111 \rangle$ -oriented linear defect in GaP, which has been studied in detail in photoluminescence via its bound exciton spectra [9]. In this case all observed electronic states of the excitons are within a few meV of the lowest state (at 2.087 eV at 2 K) and the splittings are again explained in a satisfactory manner by a moderate J-J splitting and a weak axial strain field [9]. A recent study of the COL defect in GaP with the lowest BE state at 2.1774 eV (concluded to be a $\text{Cu}_\text{I}-\text{Cu}_{\text{Ga}}-\text{Cu}_\text{I}$ complex) on the other hand, reveals a case with a much stronger effect of the axial field and also a very strong J-J splitting [10]. Similar, but even stronger effects of axial field and exchange interaction are observed for the bound exciton at 1.911 eV in GaP, tentatively ascribed to a $\langle 100 \rangle$ -oriented $\text{Cu}_\text{I}-(\text{Cu-Ga})_{\text{Ga}}$ complex [11]. Both these emission bands have been found to disappear upon Li-diffusion while new emissions are introduced.

As a continuation of these studies we report here the results of an investigation with optical spectroscopy on isoelectronic defects formed by the interaction of Cu and Li in GaP. Both these group I species are fast interstitial diffusers, and as an isolated impurity Li may only occupy interstitial sites [9,10] while the case of Cu is more uncertain. In a complex both are able to occupy a Ga-site. Doping with Li and Cu is therefore expected to create complexes involving Ga-sites and interstitial sites, combined to form neutral associates. Several different complexes may be expected, depending on which of the atoms (Cu or Li) occupies a Ga-site,

the number of each species involved, and which interstitial sites they occupy.

In this study we have observed 4 different (Cu-Li)-related bound exciton spectra, with lowest electronic transitions at 2.306 eV, 2.276 eV, 2.242 eV and 2.116 eV ($(\text{Cu-Li})_{\text{I}}$, $(\text{Cu-Li})_{\text{II}}$, $(\text{Cu-Li})_{\text{III}}$ and $(\text{Cu-Li})_{\text{IV}}$, respectively) which only occur upon doping with both Cu and Li. Detailed photoluminescence spectra are presented for these four centers, and the splitting of electronic lines in a magnetic field was also investigated. To achieve information on all electronic states, excitation spectra were recorded with a cw dye laser. It appears that the observed electronic states are fairly close together in all these centers (splitting only a few meV) indicating only moderate exchange J-J splitting for the bound exciton, and also a moderate strength of the axial field. All BE spectra are consistent with excitons binding at centers with reduced local symmetry rather than at point defect sites.

In Sec. II below the procedure of crystal preparation and doping is described. The experimental techniques for measuring optical spectra are also outlined. Sec. III contains detailed photoluminescence (PL) data at low temperature for all four Cu-Li centers. PL spectra taken at various temperatures slightly above 2 K also reveal higher electronic states in emission as well as striking differences in phonon coupling for different electronic states (particularly for $(\text{Cu-Li})_{\text{III}}$). In Sec. III Zeeman data are also presented, providing information on the electronic lines of the four Cu-Li centers observed in PL spectra. It turns out that the dominating $(\text{Cu-Li})_{\text{III}}$ spectrum consists of a triplet line and two singlets, not readily consistent with other well known bound exciton systems in GaP. The three other Cu-Li centers exhibit a triplet-singlet structure, often observed as the consequence of an axial field interacting with BE states. In Sec. IV excitation spectra for the centers are shown, giving the spectra

of excited electronic states and their relative oscillator strength. Sec. V contains a more detailed discussion on the possible identity of the different Cu-Li complexes, suggested from their electronic properties and comparison with other previously studied Cu- and Li-related iso-electronic defects.

II. Experimental

The starting material used in these investigations was either moderately doped n-type or p-type bulk liquid-encapsulated-Czochralski (LEC) grown GaP material, or epitaxial wafers. The Cu-Li doping was performed in two steps. Cu was first introduced by diffusion in the temperature range 900 - 1100 °C in a sealed evacuated ampoule, followed by rapid quenching to room temperature. This caused the COL center to appear strongly in luminescence with its characteristic orange emission [10]. Samples doped with natural Cu as well as the pure isotopes Cu^{63} and Cu^{65} were separately prepared. The second diffusion step to produce Li-doping was performed at 500 - 600 °C. Also here both Li^6 and Li^7 were used to enable the measurements of isotope shifts in characteristic emission lines. The result of this second Li doping step on optical spectra was such that the characteristic COL emission always disappeared completely, while the new Cu-Li related spectra, described in detail below, appeared. Often the previously reported $\text{Li}_\text{I}\text{-Li}_{\text{Ga}}\text{-O}_\text{P}$ spectrum with electronic ground state at 2.087 eV also appeared weakly, indicating the presence of O in most samples. None of the spectra reported here showed any shift with changes in O isotope, so the relevant complexes are believed unlikely to involve O. Li doping alone only produced the shallow DA-pair spectra involving the two inequivalent Li_I donors and the corresponding BE spectra close to the bandgap [12]. None of the Cu-Li BE spectra described in this paper are found with Li-doping alone, which further proves their association with both Cu and Li.

Photoluminescence (PL) measurements were performed either with Ar^+ or Kr^+ cw laser excitation at temperatures varying from 1.8 K up to 30 K. PL spectra were obtained with a Jarrell Ash 0.75 m double grating monochromator and with a 2 m Bausch and Lomb single grating spectrograph. Magneto-optical data were obtained with a Varian electromagnet at fields up to 3.5 T and a superconducting Thor magnet at fields up to 6 T. Excitation spectra were performed with cw dye laser excitation, mostly with narrow band detection through the 0.75 m monochromator to select out a suitable part of the spectrum. Sometimes broad band detection with a filter was employed. A grating filter was occasionally necessary on the output of the dye laser to reduce the background straylight level in cases of very weak signals.

III. Experimental results

III:1. Low Temperature Photoluminescence Spectra

In Fig. 1 is shown a typical low temperature photoluminescence (PL) spectrum from Cu-Li codoped GaP. It is dominated by four different spectra involving sharp electronic lines, and with varying degree of phonon-assisted wings at lower energies. The most shallow center $(\text{Cu-Li})_{\text{I}}$ occurs with two electronic lines L_{I}^1 and L_{I}^2 at 2.3072 eV and 2.3062 eV respectively (Fig. 1a). The sharpness and energy positions of the lines indicate that they are electronic transitions from a bound exciton complex [3]. Investigation in a magnetic field of 3.5 T shows that the lower energy line L_{I}^2 is a triplet ($J=1$) with $g = 2.2$, while the higher energy component L_{I}^1 does not split, see inset in Fig. 1a.

Rather weak phonon coupling occurs with the $(\text{Cu-Li})_{\text{I}}$ defect. In Fig. 2a,b the phonon sideband of the $(\text{Cu-Li})_{\text{I}}$ emission is shown in detail. The phonon energies and interpretations of the most prominent peaks are listed in Table I. LO phonon replicas of both electronic lines can be seen with phonon energy of 50.2 eV (LO^{T}) in agreement with earlier data on bound exciton spectra [3,13]. Two slightly weaker peaks are tentatively identi-

fied as local-mode replicas of the same two electronic lines, with a phonon energy of 52.8 meV. A second weaker local-mode replica is present 51.4 meV below the L_I^2 line (Fig. 2a). The corresponding replica of the L_I^1 component would be partly overlapping the LO^Γ replica of the L_I^2 line, and therefore hard to detect. Other weak phonon replicas within the one-phonon region of the electronic lines can also be seen in Fig. 2. The TO^X momentum conserving (MC) replicas of the two electronic lines are seen 45.2 meV below these lines. The triplet L_I^2 shows strongest coupling to the TO^X mode, whereas the coupling strength to LO^Γ appears to be about equal for both electronic transitions. Weaker components of coupling to the TO^Γ mode also seem to be present 45.7 meV below the electronic lines. An additional rather strong peak appears at 2.2695 eV, thermalizing to become stronger relative to the background at higher temperatures. This peak is not a part of the overlapping spectrum due to replicas of the nitrogen lines A and B, but probably a 37.7 meV local gap mode replica of L_I^1 . This assumption is supported by the thermalization behaviour. No corresponding replica is seen for the L_I^2 line.

A discrete peak is observed at low temperatures 41.2 meV below the L_I^2 line (Fig. 2a). This local gap mode is also responsible for a replica of the L_I^1 line partly overlapping the LO^Γ replica of the nitrogen line N_B (N_B-LO^Γ is at 2.2663 eV). Another feature that is related to L_I^2 is the 31.6 meV LA^X replica. This phonon conserves momentum in the recombination of the bound exciton in indirect gap GaP [14]. It is not seen for the higher energy singlet line, partly due to overlap with another electronic line at 2.2758 eV from the system $(Cu-Li)_{II}$. Also the coupling to a LA^X phonon is expected to be weaker for the singlet than for the triplet, as is observed for TO^X . On the other hand, a lower density of states LA component of energy 30.4 meV is observed as a weak replica of the L_I^1 line. At lower phonon energies a rather sharp line is seen at low tempera-

ture, exactly at the expected energy of a TA^X replica of L_I^2 ($TA^X=13.1$ meV). At higher temperatures the corresponding, relatively weaker replica of L_I^1 appears clearly (Fig. 2a and b). A more striking feature is the occurrence of a broad band peaking at about 2.296 eV, associated with the higher energy L_I^1 line. It seems that there is a range of quasilocalized in-band resonance phonon modes with energies about 10-12 meV coupling rather strongly to this transition.

A slight increase in temperature above 2 K has a dramatic effect on the relative line intensities of the two electronic lines in the $(Cu-Li)_I$ spectrum. Due to thermalization the higher lying singlet state becomes relatively much stronger at an increased temperature. Apparently the singlet ($J=0$) state has an appreciably higher oscillator strength, than the lower energy triplet. (A factor 10-15, see also below under Sec. III:2). A similar thermalization behaviour is observed for the phonon replicas discussed above (Fig. 2).

The second spectrum $(Cu-Li)_{II}$ consistently appearing in all Cu-Li doped samples, has an electronic line at 2.2758 eV at 2 K. A higher electronic state belonging to the same defect appears quite weak at 2.2777 eV at 2 K, but becomes relatively much stronger at a slightly higher temperature (Figs. 1 and 2). In a magnetic field of 3.5 T, the lower energy component L_{II}^2 is a triplet with $g \approx 2$, while the higher L_{II}^1 line is a singlet state. The singlet and triplet have closely similar transition probabilities in this system in contrast to the other singlet-triplet systems observed. The phonon coupling to the $(Cu-Li)_{II}$ transition appears even weaker than is the case with the shallower $(Cu-Li)_I$. A MC TA^X replica expected at 2.2627 eV is possibly seen, though extremely weak. The corresponding LA^X replica would not be seen in the region 2.244-2.245 eV where the strong electronic transitions of $(Cu-Li)_{III}$ occur. The strong and broad phonon wing of the $(Cu-Li)_{III}$ spectrum dominating at lower energies also prevents detection of optical phonon replicas associated with the $(Cu-Li)_{II}$ lines.

The third spectrum that can be consistently associated with Cu-Li codoping is often dominant, and also has a quite different appearance from the higher energy spectra $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ described above. As apparent from Fig. 1b and in more detail from Fig. 3, $(\text{Cu-Li})_{\text{III}}$ exhibits three different electronic lines in PL spectra. The lowest line L_{III}^3 occurs at 2.2419 eV, and it has a small relative oscillator strength. Therefore it is strong only when thermally favoured at the very lowest temperatures. The other two lines appear at 2.2440 eV (L_{III}^2) and at 2.2454 eV (L_{III}^1). The L_{III}^3 line is a magnetic triplet with $g = 1.85$ according to magnetic field measurements up to 6 T. This is shown in the inset of Fig. 1b, where the lowest magnetic subcomponent is strongest due to thermalization. Neither of the higher electronic lines which increase in intensity with rising temperature splits in a magnetic field of 6 T.

As already noted, the phonon coupling to the $(\text{Cu-Li})_{\text{III}}$ center is much stronger than for the two more shallow Cu-Li centers, and also complicated by the fact that the three electronic states have a very different characteristic phonon coupling. This is illustrated in Figs. 3 and 4 as well as in Table II, which contains a comprehensive list of all phonon replicas observed in the $(\text{Cu-Li})_{\text{III}}$ spectrum. The L_{III}^3 line dominates the purely electronic spectrum at the lowest temperature (2 K) in Fig. 3a. As expected for a bound exciton transition of low oscillator strength the phonon coupling is characterized by three sharp peaks at the energies of the dominant MC phonons close to the X point of the Brillouin zone in the GaP reciprocal lattice [14]. They are L_8 ($\text{TA}^{\text{X}}=13.2$ meV), L_{13} ($\text{LA}^{\text{X}}=31.5$ meV) and L_{18} ($\text{TO}^{\text{X}}=45.3$ meV).

In addition coupling of L_{III}^3 to LO^{Γ} is represented by a peak L_{21} at phonon energy 49.9 meV. Other discrete modes of a different nature also are present in Fig. 3a, such as a weak peak at about 2.2262 eV, above the TA^{X} branch, but resonant with other TA and LA branches [14]. This peak is

associated with the L_{III}^3 line. Still weaker peaks, which may be related to the lowest $(\text{Cu-Li})_{III}$ state, appear at lower phonon energies, L_4 , L_5 , L_6 and L_7 (Fig. 4a,b and Table II). Also L_4 and L_5 may be connected with an underlying pair emission. Further, the peaks L_6 and L_7 are fairly sharp, and could be a pair of electronic lines associated with an unidentified center. A sharp peak L_{10} is possibly of electronic origin, i.e. connected with a different unknown center, since an in-band resonance mode would be expected to be broader. Weak discrete peaks appear in the gap region of one-phonon energies around 2.200-2.205 eV, and a peak L_{16} appears to be related to the L_{III}^3 line. At phonon energies above the phonon branch of GaP true local modes appear. The sharpest ones are L_{23} with phonon energy 53.3 meV, L_{25} (60.4 meV) and L_{26} (63.1 meV). The last two modes involve high phonon energies, comparable to observations for Li-Li-O [9].

There is a continuum background from coupling to the acoustical phonon continuum present at lower energies. This is particularly noticeable by the decrease in emission intensity above the TA^X cut-off phonon energy, i.e. below photon energies of 2.2287 eV in Fig. 3a. It is difficult to estimate the true strength of this continuum phonon coupling for the L_{III}^3 transition, due to an overlap with the weak, broad pair spectrum responsible for the background above 2.244 eV in Fig. 3a.

At slightly higher temperatures the second electronic transition L_{III}^2 appears equally strong (Fig. 3b), to finally dominate the emission at still higher temperatures (Fig. 3c). As pointed out above, phonon coupling to the lowest triplet state L_{III}^3 and the L_{III}^2 singlet is very different. The most striking difference is that the strong contributions from the MC phonons TA^X , LA^X and TO^X observed in the phonon sideband of L_{III}^3 are very much weaker for L_{III}^2 . The broad continuum background from the acoustic spectrum appears with the singlet in a similar way as for the triplet state, with broad peaks at phonon energies close to the density of states peaks of the TA and LA branches in GaP. The LO^Γ interaction is also of similar strength for this

state as for the lowest triplet, as evidenced with the peak L_{20} in Fig. 3b and 3c.

Weak modes occur resonant with the LA band between 2.210 and 2.215 eV, and two localized gap modes L_{14} and L_{15} are prominent. Similarly, two separate true local modes are observed at phonon energies 53.3 (L_{22}) and 56.8 meV (L_{24}) (Fig.4). The energy difference between these modes and the gap modes just mentioned is similar. The low energy local mode is also the same as the one causing the L_{23} replica of L_{III}^3 (possibly the 56.8 meV local mode was not observed due to more noise in the weaker spectrum when the L_{III}^3 line is strongest). All these properties are qualitatively very similar to those observed for the Li-Li-0 bound exciton in GaP [9], with the major difference that many more true local modes appear in the Cu-Li spectrum.

It has been difficult to study the phonon coupling to the highest $(\text{Cu-Li})_{III}$ singlet state L_{III}^1 in detail, since it could not be made to dominate over the L_{III}^2 line at any temperature. A LO^Γ phonon replica L_{19} of this line is seen in Fig. 3c, with a similar coupling strength to LO^Γ phonons as for the other electronic states. No sharp momentum conserving phonon replicas of L_{III}^1 are seen in Fig. 3c, indicating similar phonon coupling as to the L_{III}^2 line. This is consistent with the fact that both singlet excited states produce allowed bound exciton recombinations compared to the rather strongly forbidden triplet transition. All above mentioned phonon replicas in the $(\text{Cu-Li})_{III}$ spectrum are summarized in Fig. 4 and Table II.

An interesting observation concerns the relative intensities of the spectra $(\text{Cu-Li})_{I-III}$ as the temperature is slightly raised above 2 K. At the lowest temperatures the PL intensities of the electronic lines of these centers are of the same order of magnitude (see Fig. 1a). At slightly elevated temperature a very strong rise of the $(\text{Cu-Li})_{III}$ spectrum is obvious in Fig. 2b when compared with Figs. 1a and 2a. The $(\text{Cu-Li})_{III}$ spectrum

gains considerably in intensity compared with the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ spectra. This is also clearly illustrated in Fig. 5, where a part of the spectrum from Fig. 1 is shown, at somewhat elevated temperature. The allowed singlet transition L_{III}^2 dominates the $(\text{Cu-Li})_{\text{III}}$ spectrum and the recombination shifts over to $(\text{Cu-Li})_{\text{III}}$ to a large extent. Apparently the recombination via $(\text{Cu-Li})_{\text{III}}$ is saturated at the very lowest temperatures due to the low transition probability of the L_{III}^3 triplet. As the temperature rises, the allowed transition L_{III}^2 , increases the recombination rate at the center, provided that the exciton capture rate is not too slow. From the strong background observed in excitation spectra (to be described below under Sec. III:2), we know that the capture process for excitons to $(\text{Cu-Li})_{\text{III}}$ is strong, as well as the transfer of excitons from $(\text{Cu-Li})_{\text{I}}$. Also, the $(\text{Cu-Li})_{\text{III}}$ center is favoured at high temperatures partly because the exciton localization energy is large compared with the other centers. In the thermal quenching of luminescence from $(\text{Cu-Li})_{\text{I}}$ at 20 K, the tunneling transfer will be assisted by phonon participation as was observed for Bi spectra in GaP [15].

The fourth spectrum in Fig. 1, called $(\text{Cu-Li})_{\text{IV}}$, which has consistently appeared with Cu-Li codoping, has an electronic line L_{IV}^2 at 2.1158 eV at 2 K. Only this electronic line appears strongly in low temperature PL spectra. The line is a triplet according to measurements in magnetic field up to 6 T. The splitting of the three components shown in Fig. 6c corresponds to a g value slightly less than 2 ($g \approx 1.95$) and the relative intensities of the peaks are consistent with strongly thermalized population of the initial states. For this system higher electronic states are split off much further away in energy than for the more shallow $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ centers. Actually, there is a much stronger electronic state at 2.1228 eV, as evident from PLE spectra included in Fig. 6a (see below Sec. III:2). This higher state will only be weakly thermally populated in PL experiments in the range 2-20 K covered in these experiments, but still it can be seen

weakly in Fig. 6 as a consequence of its much larger oscillator strength. The relative intensity of the $(\text{Cu-Li})_{\text{IV}}$ spectrum to the $(\text{Cu-Li})_{\text{III}}$ spectrum shows similar temperature development as the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ spectra. This is obvious in Fig. 6b, where the $(\text{Cu-Li})_{\text{IV}}$ spectrum has disappeared while $(\text{Cu-Li})_{\text{III}}$ is still very strong

The phonon coupling strength of the 2.1158 eV line of $(\text{Cu-Li})_{\text{IV}}$ is much weaker than for $(\text{Cu-Li})_{\text{III}}$, again putting the $(\text{Cu-Li})_{\text{IV}}$ center in a similar category to $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ despite the much larger localization energy of this bound exciton. It is therefore concluded that the $(\text{Cu-Li})_{\text{IV}}$ center must contain a rather weakly bound electronic particle. Due to the background from the multiphonon wing of the $(\text{Cu-Li})_{\text{III}}$ spectrum it is difficult to estimate the strength of phonon coupling for $(\text{Cu-Li})_{\text{IV}}$. There is a continuum background with broad peaks at approximately 11 meV and 26 meV below the electronic line, typical for the interaction with the acoustic phonon continuum as seen in the $(\text{Cu-Li})_{\text{III}}$ spectrum (Fig. 3). A distinct but rather weak quasilocalized phonon mode is seen with phonon energy of about 19 meV. In the range of optical phonons we have in all samples a superposition of the structured spectrum of the $\text{Li}_{\text{I}}\text{-Li}_{\text{Ga}}\text{-O}_{\text{P}}$ center, due to the presence of O in our samples. It is therefore difficult to estimate the strengths of possible replicas of the 2.1158 eV line in this region.

III:2. Excitation Spectra

To gain information on the existence of further electronic excited states beyond the range of thermal population obtainable in PL spectra, absorption spectra for the (Cu-Li) centers are necessary. Since the concentration of the defects binding the excitons under study appears to be rather low and the oscillator strengths are also weak, the only feasible way of achieving such information is from photoluminescence excitation

(PLE) spectra, employing a cw dye laser. To avoid detection of excitation light, it is in practice necessary to detect a part of the emission, characteristic for a particular center, displaced some suitable distance away from the excitation region to be covered. For that reason the two high energy emissions $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ in Fig. 1 are not suitable for direct PLE measurements, since the phonon assisted part of the spectrum is too weak in both cases. For $(\text{Cu-Li})_{\text{I}}$ it was possible to obtain indirectly a (non-selective) PLE-spectrum by detecting the intensity of the $(\text{Cu-Li})_{\text{III}}$ spectrum, excited via excitation transfer from $(\text{Cu-Li})_{\text{I}}$ (Fig. 7). The no-phonon transition to the 2.3062 eV triplet ground state is just barely seen below the 2.3072 eV transition. The measured difference in oscillator strength is about a factor 10-15 in favour of the 2.3072 singlet state.

Other weaker and slightly broader states appear between the L_{I}^1 line and the S-donor exciton line in Fig. 7. The photon energies of these states are 2.3081 eV and 2.3091 eV, respectively. Actually, very weak components appear at approximately these energies also in PL spectra, but these components do not seem to thermalize with the $(\text{Cu-Li})_{\text{I}}$ lines in PL data (Fig. 2). We therefore conclude that these additional electronic states are not related to the $(\text{Cu-Li})_{\text{I}}$ spectrum. They could be due to components from a N-acceptor pair spectrum evidently present in the PL spectra of Figs. 1 and 2 [16].

Similar excitation transfer PLE spectra were not obtainable for the $(\text{Cu-Li})_{\text{II}}$ spectrum. Therefore, we have no information from absorption data on this center. The weaker intersite exciton transfer is most likely due to the larger exciton localization energy of $(\text{Cu-Li})_{\text{II}}$ as well as the smaller concentration of this center, as apparent when the luminescence intensities at low temperature are compared. This is even more obvious at higher temperature, when the L_{I}^1 component is very strong, indicating a rather large oscillator strength compared with the $(\text{Cu-Li})_{\text{II}}$ components. We just

note that PL data at elevated temperature in this case do not reveal any electronic states in addition to the triplet-singlet pair described in Sec. III:1.

For the $(\text{Cu-Li})_{\text{III}}$ center the PLE spectrum can be obtained more directly, since a broad phonon wing is present in the PL spectrum, allowing the detection of PLE spectra. The result of such a measurement is shown in Fig. 8, where a strong background due to dominant exciton or carrier capture (via two-step excitation) is subtracted. The transition to the weak triplet ground state at 2.2419 eV does not appear in the PLE spectrum. This is consistent with the PL data (Fig. 3c), where the L_{III}^3 transition can be estimated to be at least a factor 100 weaker than the singlet L_{III}^2 . Such weak transitions cannot be seen in the PLE-data. Three strong allowed transitions are positively identified in Fig. 8, at 2.2440 eV (A_{III}^2), 2.2454 eV (A_{III}^1) and 2.2510 eV (A_{III}^4) at 2 K. Their relative oscillator strengths are approximately 1:0.7:0.6, respectively. Unfortunately, the lines are too weak to allow Zeeman data to be taken in PLE. Therefore, the multiplicity of the A_{III}^4 transition at 2.2510 eV is not established. A slightly wavy background is present from the dye laser straylight, but the TA and LA density of states maxima are identified as noted in the figure.

For the $(\text{Cu-Li})_{\text{IV}}$ center it was again possible to obtain directly a PLE spectrum via PL detection in the weak but broad phonon assisted part of the spectrum (Fig. 6a). As seen in the inset of Fig. 6a, the transition to the BE ground state is not detectable in PLE spectra. The only peak seen in absorption is at 2.1228 eV (about 7 meV above the BE ground state) corresponding to L_{IV}^1 in Fig. 6a. Zeeman data were not obtainable for this peak, but it is most likely that this is again a triplet-singlet pair as observed for the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ systems. For the $(\text{Cu-Li})_{\text{IV}}$ system the oscillator strength of transitions to the excited 2.1228 state is at least 20 times larger than to the 2.1158 eV ground state.

IV. Discussion

IV:I. Models for Identity and Electronic Structure of the Centers.

The main reason for assigning all four bound exciton spectra described above to Cu-Li centers is the evidence from doping experiments. These always correlated the observed spectra with a similar doping procedure, where Cu-diffusion at high temperatures (900-1100 °C) is followed by Li-diffusion at 600-650 °C. The centers $(\text{Cu-Li})_{\text{I-IV}}$ have never been observed in GaP material which is not deliberately Li-doped. Further, in Li-doped material which is not previously Cu-doped these centers are always absent. The dominant BE spectra characteristic for GaP after Cu-diffusion at high temperatures are the COL emission at 2.1774 eV [10] and the 1.911 eV emission [11]. Both these emissions have been attributed to complexes containing inequivalent Cu atoms, Cu_{I} and Cu_{Ga} respectively. The latter is established to have a $\langle 100 \rangle$ -oriented symmetry axis in agreement with a linear complex containing Ga_{I} in addition to Cu, while the COL defect shows a complicated coupling to the lattice vibrations, suggesting a complex of three Cu atoms [10,11].

These two Cu-related emission bands vanish as a consequence of the Li diffusion (600-650 °C/60 min), while the four new spectra $(\text{Cu-Li})_{\text{I-IV}}$ appear with varying relative strength. This is an indication of a tendency for Cu and Li to pair in the Li-diffusion step. The Li-Li-O spectrum [9] has also been observed after Li-doping, with intensities ranging from strong (after Li-diffusion at 400 °C during 15h [7]) to the emission being undetectable or extremely weak. The latter is most often the case for our samples, indicating a small O-concentration, rather than unfavourable conditions for formation of the Li-Li-O centers. In the temperature range of the Li diffusions (600-650 °C) the COL and 1.911 eV emissions are expected to be quenched even in vacuum [18]. The more unstable 1.911 eV defect, at least, is believed to dissociate at this relatively low temperature, but also the COL intensity decreases upon heat treatment below 800 °C. Actually this latter emission shows a complex annealing behaviour with an intensity

maximum around 800 °C [18]. Since Cu_I is highly mobile by an interstitial diffusion mechanism, it might break up from the COL complex at rather low temperatures, and thus cause the observed thermal quenching of that emission. Consequently, we assume the presence of Cu_I donors under the Li diffusion as well as the presence of the Cu acceptor Cu_{Ga} and possibly smaller complexes such as $\text{Cu}_I\text{-Cu}_{\text{Ga}}$. Li also diffuses rapidly via an interstitial mechanism [12]. An isolated double Li_{Ga} acceptor has not been identified, and this may also be true for the Cu_{Ga} double acceptor [10]. Both Li_{Ga} and Cu_{Ga} are, on the other hand, found as parts of complexes, such as the $\text{Li}_I\text{-Li}_{\text{Ga}}\text{-O}_P$ [9] and the COL [10].

Given the diffusion procedure described above, several possibilities of forming neutral complexes of Cu and Li atoms exist. In addition to defect reactions, where a Li atom directly replaces a Cu atom in a neutral Cu-complex, the mobile Li_I^+ donors (ionized at these temperatures) may combine with a charged acceptor complex of Cu atoms influenced by the Coulomb attraction, and the Cu_I^+ donors may pair with the Li acceptor complex in a similar way. Also, a pair of interstitial donors can be assumed to combine with an isolated double acceptor of the other type if these exist. Such centers can be classified as isoelectronic molecular centers, having no electronic spin in the ground state. The observed multiplicity of the different electronic BE lines, with an overall triplet-singlet pair character, is consistent with such spin-free final states of the PL emission. The possibility of two or more particles in the ground state pairing off to give $S = 0$ is not attractive due to strong Auger processes, which should severely weaken the corresponding luminescence. For the same reason complexes containing a Cu atom with an open d-shell configuration seem improbable [19]. It is necessary to measure the decay time to rule out these latter configurations with certainty, however.

In our hypothesis of neutral isoelectronic centers we suggest the identity of the different Cu-Li centers on basis of the evidence so far

presented. We tentatively attribute the two most deeply bound excitons $(\text{Cu-Li})_{\text{III}}$ and $(\text{Cu-Li})_{\text{IV}}$ to centers involving Cu on a Ga site, and the two shallower ones $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ to centers with Li on a Ga site. This arrangement is suggested from our knowledge of the binding energies of acceptor-like Cu and Li complexes. The Cu-related acceptors have binding energies ≥ 500 meV [20], whereas a Cu-Li acceptor associate, which probably involves Li_{Ga} has a binding energy $E_{\text{A}} = 116$ meV. This energy is deduced from a pair emission peaking at about 2.17 eV, which involves a deeper acceptor than the usual shallow DA pairs, provided that the donor is shallow [21]. This pair emission has only been observed in crystals showing strong Li and Cu-Li spectra, upon diffusion with both Cu and Li. No signs of the emission is observed after Li-diffusion alone.

A comprehensive set of defects for the two more shallow (Cu-Li) centers is a $\text{Li}_{\text{I}}\text{-Li}_{\text{Ga}}\text{-Cu}_{\text{I}}$ complex giving the $(\text{Cu-Li})_{\text{I}}$ BE emission, and a $\text{Cu}_{\text{I}}\text{-Li}_{\text{Ga}}\text{-Cu}_{\text{I}}$ complex binding $(\text{Cu-Li})_{\text{II}}$ exciton. Both defects are probably $\langle 100 \rangle$ -oriented, since this direction seems to offer the most spacious interstitial sites for two interstitial atoms [22]. The larger BE localization energy E_{BX} for a center containing no $\text{Li}_{\text{I}}\text{-Li}_{\text{Ga}}$ pair is consistent with a simple electrostatic model of the repulsion energy between these donor- and acceptor-like entities, since the radius of the Li ion is much less than for Cu. If instead a Cu_{Ga} acceptor is involved in a complex with two interstitial atoms a deeper center is expected to result, as is the case for $(\text{Cu-Li})_{\text{IV}}$, which we attribute to a $\text{Cu}_{\text{I}}\text{-Cu}_{\text{Ga}}\text{-Li}_{\text{I}}$ defect. The $(\text{Cu-Li})_{\text{III}}$ center may then be attributed to $\text{Li}_{\text{I}}\text{-Cu}_{\text{Ga}}\text{-Li}_{\text{I}}$ defect, with smaller BE localization energy than $\text{Cu}_{\text{I}}\text{-Cu}_{\text{Ga}}\text{-Li}_{\text{I}}$ for the reason already noted. The fact that this center contains two Li atoms is also consistent with the complexity of the Li local mode structure in the $(\text{Cu-Li})_{\text{III}}$ spectrum in Fig. 4. The difference in the BE localization energy E_{BX} between the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{IV}}$ defects is 190 meV, assigned to the tighter binding of holes to complexes containing Cu_{Ga} instead of Li_{Ga} . It is not easy to estimate the corresponding binding energies of the acceptor associates, since the repulsion terms

depend on exact positions of the ions and the electrostatic screening. In fact the detailed defect symmetry of the proposed centers is not yet revealed. However, according to the general electrostatic model the exciton should be more tightly bound to $(\text{Cu-Li})_{\text{III}}$ than to $(\text{Cu-Li})_{\text{II}}$, since the former is assumed to contain Cu_{Ga} . On the other hand, the presence of two Li_{I} atoms gives stronger repulsion than that of two Cu_{I} , hence, the difference in E_{BX} is only 34 meV between these centers. Similarly, E_{BX} for $(\text{Cu-Li})_{\text{IV}}$ is 126 meV larger than for $(\text{Cu-Li})_{\text{III}}$ due to the presence of the larger Cu_{I} in the deeper center, replacing a Li_{I} in $(\text{Cu-Li})_{\text{III}}$.

The three centers $(\text{Cu-Li})_{\text{I,II,IV}}$ all show similar sets of electronic lines, in agreement with a recombination from a lowest spin-triplet to a spin-free ground state and also from a higher singlet state which becomes thermally populated at slightly raised temperature. The lowest line dominates only at the very lowest temperatures, below 2 K. In a magnetic field the lowest magnetic subcomponents are also favoured by thermalization (Figs. 1a and 6b). In PLE measurements none of these triplets is observed, while the corresponding singlets are seen except for the $(\text{Cu-Li})_{\text{II}}$ defect. This center seems to have too low a concentration to be detectable in PLE, and also it has no observable phonon wing suitable for detection. The transitions described above agree very well with spin-forbidden transitions from $S=1$ BE triplets, observed in several other cases [10,11]. A common feature for the previously studied triplet-singlet pairs is a strong axial field from the local arrangement of the defect atoms. This crystal field splits the hole states and thereby quenches the spin orbit coupling, resulting in the observed BE states through combination of two spin ($S=1/2$) particles [3]. In case of compressive strain field the triplet-singlet pair is the lowest pair of bound exciton states. According to our observations, the triplet state is at lowest energy. Also, transitions to the spin-free ground state are forbidden by a spin selection rule and dominating only when heavily favoured by thermalization. Additionally the thermalization between magnetic subcomponents observed for

the triplet in magnetic field also shows that the splitting occurs in the initial state of the transition.

The exchange splitting between the $J=1$ and $J=0$ components of the BE states is about the order of magnitude usually found in GaP [3]. It increases with the exciton localization energy at the defect from 1.0 meV for $(\text{Cu-Li})_{\text{I}}$ through 1.9 meV for $(\text{Cu-Li})_{\text{II}}$ to 7 meV for the much deeper BE $(\text{Cu-Li})_{\text{IV}}$. With increasing binding energy of the excitons at the defects the localization of the electron and hole wavefunctions may cause a larger overlap of these, leading to a stronger exchange interaction between the particles of the bound exciton. However, an exchange splitting of 7 meV is in fact very large compared to other deeply bound excitons, e.g. the Li-Li-O exciton. We suggest that the unusually large exchange interaction is related to the presence of a $\text{Cu}_{\text{I}}\text{-Cu}_{\text{Ga}}$ in the $(\text{Cu-Li})_{\text{IV}}$ center. This is the only center in the postulated set of defects involving such a pair, which is also found in the COL center and the 1.911 eV center. Both these latter centers show very much larger exchange splittings [10,11].

No obvious alternative models for the quenching of the hole angular momentum seem relevant for the bound excitons. In contrast to e.g. Bi in GaP [15] which shows a quenching of the spin-orbit coupling caused by strong Jahn-Teller coupling (the well known Ham effect [23]), the phonon coupling to these Cu-Li bound excitons is weak. In addition the $J=2$ state of the Bi exciton splits into a triplet (with anisotropic splitting) and a doublet upon Jahn-Teller coupling, as is the case for a strong cubic symmetry as well. Also the singlet character of the higher energy components is well established for $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{III}}$ at least, and the triplets split isotropically in magnetic field as far as can be determined.

The dominating $(\text{Cu-Li})_{\text{III}}$ emission differs in some aspects from the above mentioned BE spectra, exhibiting a more complex structure of electronic lines than these. A set of four electronic lines is observed. The highest one, 9 meV above the lowest BE state, is only detectable in PLE measurements.

The phonon coupling associated with these transitions is stronger than other Cu-Li emissions show, differing as the thermal population of the BE states favours the different transitions. The lowest state is a triplet, and it splits symmetrically and approximately isotropically in magnetic field, with a g value close to the electron value. Obviously, transitions between the triplet and the ground state are forbidden also in this case, as illustrated at higher temperatures when the lowest component vanishes as the higher ones appear. Also, a strong coupling to MC phonons at the X point of the Brillouin zone indicates that transitions from this state mainly occur through phonon coupling, and only when the state is heavily favoured by thermalization. Both higher components are singlets, whereas no magneto-optical information on the fourth components was obtainable in the PLE measurements. The lowest singlet-triplet pair of this BE has a JJ-splitting of 2.1 meV, if we consider this pair as separately resulting from the combination of two spin particles in a strong compressive axial field.

In a uniaxial strain field the fourfold degenerate Γ_8 states uppermost in the valence band split into two Kramer doublets $|3/2, \pm 3/2\rangle$ and $|3/2, \pm 1/2\rangle$ (in the usual $|j, m_j\rangle$ notation). The split-off valence band state $|1/2, \pm 1/2\rangle$ remains doubly degenerate in an axial field. Through strain induced mixing of the two hole states with $m_j = \pm 1/2$ the orbital contribution to these bound hole wavefunctions is quenched. Upon coupling to a Γ_6 electron a singlet-triplet configuration of the bound exciton states results [3]. GaP is an indirect semiconductor with a set of equivalent conduction band minima near the X point of the Brillouin zone. It is well known that pseudopotential difference between Ga and P splits the X minima into X_1 and X_3 subminima [24]. Further, for electron bound at the electron attractive group V sites the $1s$ ground state derived from the X_1 minima splits into a lowest $1sA_1$ state and a higher $1sE$ state by the valley-orbit splitting. With spin included the notations are Γ_6 and Γ_8 , respectively.

For electrons bound at the less electron attractive group III site the wavefunction possesses nodes in the Bloch component instead of antinodes on the group V sites. Therefore the $1sT_2$ ground state derived from the X_3 conduction band minima is unaffected by the valley orbit splitting. When spin is included a Γ_7 ground state and a higher Γ_8 state result (the spin-valley interaction). The camel's back structure is neglected in this description [24]. The degeneracy of the Γ_8 electron states can be lifted in a uniaxial strain field. For a general direction of the axial field the Γ_8 state splits into two doublets, since the equivalence of the conduction band valleys is destroyed. Only the $\langle 111 \rangle$ direction is equivalent for the set of $\langle 100 \rangle$ conduction band minima. Therefore, the effect of the local crystal field on the electron as well as on the hole states should be considered for certain combinations of crystal field and spin-orbit coupling.

The COL and 1.911 eV centers [10,11,20] are clearly quite different from normal neutral isoelectronic traps (in the Hopfield-Thomas Lynch model [7]). Both hole and electron must interact strongly with the central cell of the center. This is plausible only if strain plays a major role in the binding rather than pseudopotential differences between host and substituent. If the local strain field is compressive and large, the valence band states will be split to provide the essentially pure spin hole states observed for the COL and 1.911 eV centers. If the strain is not purely $\langle 111 \rangle$ -oriented the conduction band states will be split in the local field also. In view of the large exchange splitting observed for these bound excitons there must be a strongly attractive potential for the electron as well as the hole, to give the required large electron-hole overlap at the core of the associates. In a resulting non-HTL model for the binding of the exciton the electron binding mainly derives from those subcomponents of the conduction band whose energies are lowered by the local strain field. The effect of replacing some of the Cu_I atoms in the Cu complexes by Li_I is equivalent to reducing the local strain field. Since the local binding of the electron derives

mainly from the strain field, whereas the hole is bound both by the pseudo-potential difference and the strain field, the electron states will be affected more than the hole states. Thus, we argue that the L_{III}^1 singlet might come from the upper set of electron subbands, which are only moderately split by this axial field. The corresponding triplet is obscured by the lower singlet transition and never dominates, since it cannot be favoured by thermalization as can L_{III} . Recently a 1s excited state of an exciton bound to the neutral S_p donor in GaP has been observed [25]. The excited state corresponds to the first electron associated with the $1s(\Gamma_6)$ state and the second one associated with the $1s(\Gamma_8)$ state. A stress-induced absorption line reveals the existence of this state.

We shall not speculate too much on the origin of the fourth component A_{III}^4 , revealed in PLE measurements. A possible assignment is that it is related to the $m_j = \pm 3/2$ split-off hole state. This interpretation requires that a small strain splitting of the hole states would be compatible with a nearly isotropic hole splitting. Another possibility is that the A_{III}^4 component is derived from the corresponding split-off electron states.

Finally an analogous spectrum in GaP:Sb will be briefly discussed [26]. This BE spectrum shows four no-phonon lines at an exciton localization energy of about 40 meV. The group of lines consists of two sets of triplet-singlet pairs, with the triplets at lowest energy in each set. The spacing between the sets is about 4.5 meV. This electronic structure has been a long-standing mystery. We propose that it can be explained in terms of the model outlined above. There, the splitting of 4.5 meV between the two triplet-singlet sets may be attributed to the splitting of the conduction subbands in the local strain field. Accordingly, the isoelectronic substitute is believed to be a pair of nearest neighbours Sb_p atoms, oriented along a $\langle 110 \rangle$ direction.

The fact that the exchange splitting of the upper pair is smaller than for the lower pair, and also that the former shows a much higher intensity of the triplet [26], are qualitatively consistent with the model. The smaller exchange interaction for the upper set is a consequence of a reduced electron-hole overlap due to less localized wavefunctions. This in return reduces the quenching of the orbital angular momentum of the hole states and thus relaxes the spin selection rule for the transitions.

V. Conclusions

The four BE emission spectra observed in GaP after Cu diffusion (900-1100 °C/1 hr) with rapid quenching to room temperature, and a subsequent Li diffusion (500-600 °C/1hr) have been studied. Models for the identity of these centers are deduced from the electronic structure, details of the vibrational sidebands and the evidence from the doping procedure.

The $(\text{Cu-Li})_{\text{I}}$ center with a triplet at 2.3062 eV as a BE ground state and exchange splitting $\Delta_{\text{JJ}} = 1.0$ meV is attributed to a neutral complex of three atoms, $\text{Li}_{\text{I}}\text{-Li}_{\text{Ga}}\text{-Cu}_{\text{I}}$. This identification is suggested on basis of the requirement of a neutral and spin-free final state of the BE recombination for a triplet-singlet pair of BE states to be formed. Additionally, it is required that the orbital angular momentum of the hole states involved is quenched in the axial strain field postulated for this defect geometry. The resulting BE triplet then splits isotropically in magnetic field as observed.

Similar arguments apply to the other three complexes. A $\text{Cu}_{\text{I}}\text{-Li}_{\text{Ga}}\text{-Cu}_{\text{I}}$ complex is suggested as the $(\text{Cu-Li})_{\text{II}}$ center, binding an exciton with a BE ground state at 2.2758 eV and $\Delta_{\text{JJ}} = 1.9$ meV. A larger exciton localization energy for this center is consistent with simple electrostatic arguments concerning the repulsion between the donor- and acceptorlike parts of the complex. The larger Cu_{I} atom is expected to give a weaker repulsion than the corresponding Li_{I} in the $(\text{Cu-Li})_{\text{I}}$ center, hence the exciton is more

tightly bound to the $(\text{Cu-Li})_{\text{II}}$ center.

The dominant emission $(\text{Cu-Li})_{\text{III}}$ is believed to involve a Cu_{Ga} double acceptorlike entity, balanced by two Li_{I} interstitial donors to form a $\text{Li-Cu}_{\text{Ga}}\text{-Li}_{\text{I}}$ complex. The complex Li local mode structure of the phonon sideband, with high energy local modes corresponding to both Li^6 (56.8 meV) and Li^7 (53.3 meV), supports this view. A second singlet is also observed in this spectrum, 1.4 meV higher in energy than the first one. It is concluded that this unusual electronic structure is a result of a splitting of the electron as well as the hole states in the local strain field of the defect. This means that there is a strain contribution to the exciton localization energy from both the electron and hole binding. Usually, in such situations the exciton binding derives from the components of the bound states whose energies are lowered by the strain field and only one electron state is believed to be involved in most cases.

A hitherto unexplained double set of triplet-singlet pairs of BE lines in GaP:Sb [25], presumably bound to $\langle 110 \rangle$ -oriented nearest neighbour Sb_{p} pairs, is postulated to be analogous to the $(\text{Cu-Li})_{\text{III}}$ spectrum. In the case of GaP:Sb the stronger axial field corresponding to the larger splitting observed, makes the second triplet observable, whereas it is overlapping the strong singlet L_{III}^2 in the $(\text{Cu-Li})_{\text{III}}$ spectrum.

The fourth spectrum $(\text{Cu-Li})_{\text{IV}}$ is deepest and deduced to involve Cu_{Ga} in a $\text{Cu}_{\text{I}}\text{-Cu}_{\text{Ga}}\text{-Li}_{\text{I}}$ defect. Again, the substitution of a Cu_{I} atom for a Li_{I} reduces the repulsion, and this center binds the exciton more tightly than the $(\text{Cu-Li})_{\text{III}}$ does. The exchange interaction of the $(\text{Cu-Li})_{\text{IV}}$ center is larger than expected for an exciton with this binding energy ($\Delta_{\text{JJ}} = 7$ meV). It is suggested that this may be related to the presence of two Cu-atoms in the defect. A very strong exchange interaction has been observed for defects containing two or more Cu atoms [10,11,20].

Finally, it is concluded that more information is needed to confirm the identities of the centers $(\text{Cu-Li})_{\text{I-IV}}$ suggested here. ODMR signals have not been detectable for any of these systems, and Zeeman measurements cannot

resolve the small degree of anisotropy in the magnetic splitting of the triplets. Hence, the defect symmetry is still uncertain. Also, isotope doping with Li^6 and Li^7 can probably reveal the number and positions of Li atoms in the defects, particularly in the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{III}}$ spectra which show local modes of Li motion.

References

1. S.T. Pantelides, Rev. Mod. Phys. 50, 797 (1978)
2. J.A. van Vechten in Handbook of Semiconductors, Vol. 3, Materials, Properties and Preparation, Ed. S.P. Keller (North Holland, Amsterdam 1980, Ch.1)
3. P.J. Dean and D.C. Herbert in Topics in Current Physics, Vol. 14, Excitons, Ed. K. Cho (Springer Verlag, Berlin 1979), pp 55-182
4. T.N. Morgan, B. Welber and R. N Bhargava, Phys. Rev. 166, 751 (1968)
5. C.H. Henry, P.J. Dean and J.D. Cuthbert, Phys. Rev. 166, 754 (1968)
6. E. Cohen and M.D. Sturge, Phys. Rev. B 15, 1039 (1977)
7. J.J. Hopfield, D.G. Thomas and R.T. Lynch, Phys. Rev. Lett. 17, 312 (1966)
8. J. van W. Morgan and T.N. Morgan, Phys. Rev. B 1, 739 (1970)
9. P.J. Dean, Phys. Rev. B 4, 2596 (1971)
10. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, unpublished
11. H.P. Gislason, B. Monemar, P.J. Dean, D.C. Herbert, S. Depinna, B.C. Cavenett and N. Killoran, unpublished
12. P.J. Dean, Proc. Int. Conf. on Luminescence, Leningrad 1972, Ed. F. Williams (Plenum Press, 1973) p. 538
13. P.J. Dean, R.A. Faulkner, S. Kimura and M. Ilegems, Phys. Rev. B 4, 1926 (1971)
14. J.L. Yarnell, J.L. Warren, R.G. Wenzel and P.J. Dean, Neutron Inelastic Scattering 1, 301 (Vienna 1968)
15. P.J. Dean, J.D. Cuthbert and R.T. Lynch, Phys. Rev. 179, 754 (1969)
16. R.A. Street and P.J. Wiesner, Phys. Rev. B 14, 632 (1976)
17. R.N. Bhargava, S.K. Kurtz, A.T. Vink and R.C. Peters, Phys. Rev. Letters 27, 183 (1971)
18. G.M. Blom and R.N. Bhargava, J. Crystal Growth 17, 38 (1972)
19. D.J. Robbins and P.J. Dean. Advances in Physics 27, 499 (1978)
20. P.J. Dean, B. Monemar, H.P. Gislason and D.C. Herbert, Proc. 1981 ICL, Berlin, to be published in J. Luminescence

21. B. Monemar, H.P. Gislason, M.E. Pistol and P.J. Dean, unpublished
22. J.W. Corbett and J.C. Bourgoin in Point Defects in Solids, Vol. 2
Ed. J.H. Crawford, Jr. and L.M. Slifkin (Plenum Press, New York 1975)
ch. 1
23. T.N. Morgan, J. Luminescence 1,2, 420 (1970)
24. P.J. Dean, W. Schairer, M. Lorenz and T.N. Morgan, J. Luminescence 9,
343 (1974)
25. P. Merle, B. Archilla, J. Camassel and H. Matheieu, Solid State Commun 31,
205 (1979)
26. P.J. Dean, R.A. Faulkner and E.G. Schönherr, Proc. Int. Conf. Phys.
Semicond., Cambridge 1970 (USAEC, Oak Ridge, Tenn., 1970) p.286

TABLE I. Photon energies of the electronic transitions in PL spectra of the $(\text{Cu-Li})_{\text{I}}$, $(\text{Cu-Li})_{\text{II}}$ and $(\text{Cu-Li})_{\text{IV}}$ emissions. For the $(\text{Cu-Li})_{\text{I}}$ emission the energies of the most significant phonon replicas of L_{I}^1 and L_{I}^2 are listed in separate columns.

Notation	Photon energy eV	Energy from L_{I}^1 meV	Difference from L_{I}^2 meV	Interpretation
L_{I}^1	2.3072	0		J=0 singlet
L_{I}^2	2.3062	1.0	0	J=1 triplet
	2.2941	13.1		
	2.2931		13.1	TA^{x} MC
	2.2768	30.4		LA mode
	2.2746		31.6	LA^{x} MC
	2.2695	37.7		
	2.2660	41.2		
	2.2650		41.2	
	2.2620	45.2		
	2.2610		45.2	TO^{x} MC
	2.2615	45.7		
	2.2605		45.7	TO^{Γ}
	2.2570	50.2		
	2.2560		50.2	LO^{Γ}
	2.2548		51.4	local mode
	2.2544	52.8		
	2.2534		52.8	local mode
L_{II}^1	2.2777			J=0 singlet
L_{II}^2	2.2758			J=1 triplet
L_{IV}^1	2.1228			electronic line
L_{IV}^2	2.1158			J=1 triplet

TABLE II. Energy positions of the electronic transitions and the strongest phonon replicas in the (Cu-Li)_{III} PL spectrum. Phonon energies are also listed for phonons coupling to the three lines L_{III}^1 , L_{III}^2 and L_{III}^3 .

Notation	Photon energy eV	ΔE meV	ΔE meV	ΔE meV	Interpretation
L_{III}^1	2.2454	L_{III}^1			J=0 singlet
L_{III}^2	2.2440		L_{III}^2		J=0 singlet
L_{III}^3	2.2419			L_{III}^3	J=1 triplet
L_4	2.2385			L_4 3.4	pair line (?)
L_5	2.2362			L_5 5.7	pair line (?)
L_6	2.2307				electronic (?)
L_7	2.2299				electronic (?)
L_8	2.2287			L_8 13.2	TA ^x MC
L_9	2.2214				electronic (?)
L_{10}	2.2200				electronic (?)
L_{11}	2.2190		L_{11} 25.0		
L_{12}	2.2172		L_{12} 26.8		
L_{13}	2.2104			L_{13} 31.5	LA ^x MC
L_{14}	2.2075		L_{14} 36.5		gap mode
L_{15}	2.2039		L_{15} 40.1		gap mode
L_{16}	2.2018			L_{16} 40.1	
L_{17}	2.1982		L_{17} 45.8		T0 ^Γ
L_{18}	2.1966			L_{18} 45.3	T0 ^x MC
L_{19}	2.1954	L_{19} 50.0			
L_{20}	2.1940		L_{20} 50.0		L0 ^Γ
L_{21}	2.1920			L_{21} 49.9	
L_{22}	2.1907		L_{22} 53.3		local mode (Li ⁷)
L_{23}	2.1886			L_{23} 53.3	
L_{24}	2.1872		L_{24} 56.8		local mode (Li ⁶)
L_{25}	2.1815			L_{25} 60.4	local mode
L_{26}	2.1788			L_{26} 63.1	local mode
L_{27}	2.1440		L_{27} 100.0		2 L0 ^Γ

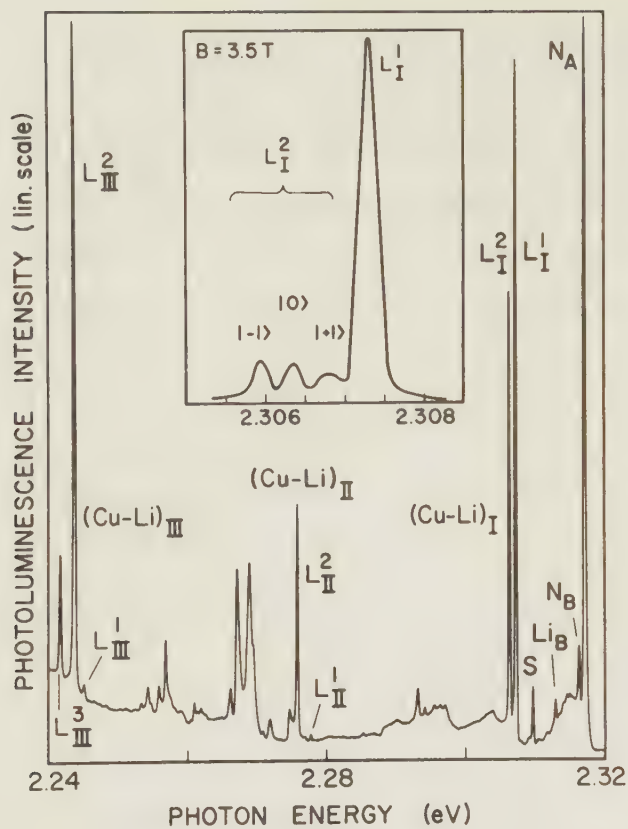


Fig. 1a. Low temperature PL spectrum (2 K) of GaP diffused with Cu and Li, excited with the 5145 Å Ar⁺ laser line. The groups of electronic lines marked (Cu-Li)_{I-III} are consistently present after such doping. In the inset the electronic lines of the (Cu-Li)_I spectrum are shown in magnetic field B=3.5 T. The L¹_I line does not split while the L²_I line splits into three components in magnetic field, corresponding to an isotropic g value, g=2.2. Similarly the L²_{II} line splits into three components in magnetic field, but the L¹_{II} line shows no splitting.

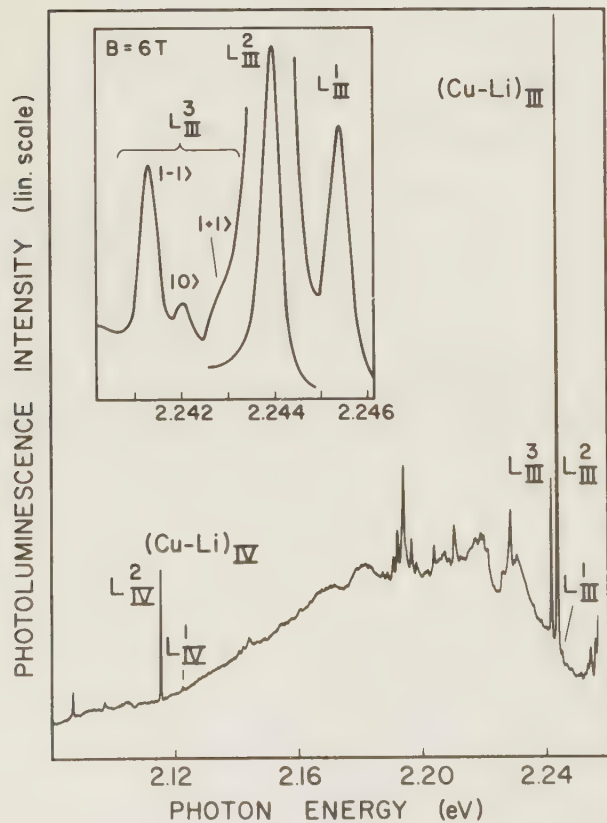


Fig. 1b. Low energy PL spectrum of the same crystal as in Fig. 1a, showing the (Cu-Li)_{III} and (Cu-Li)_{IV} emissions at 2 K. In the inset the electronic lines L¹⁻³_{III} are shown in magnetic field B=6 T. The L³_{III} line is a triplet with an isotropic value g=1.85, showing thermalization between the magnetic subcomponents. The L¹_{III} and L²_{III} lines are singlets. In the (Cu-Li)_{IV} spectrum the L²_{IV} line is an isotropic triplet with g=1.95. No magneto-optical information was obtainable for the L¹_{IV} component.

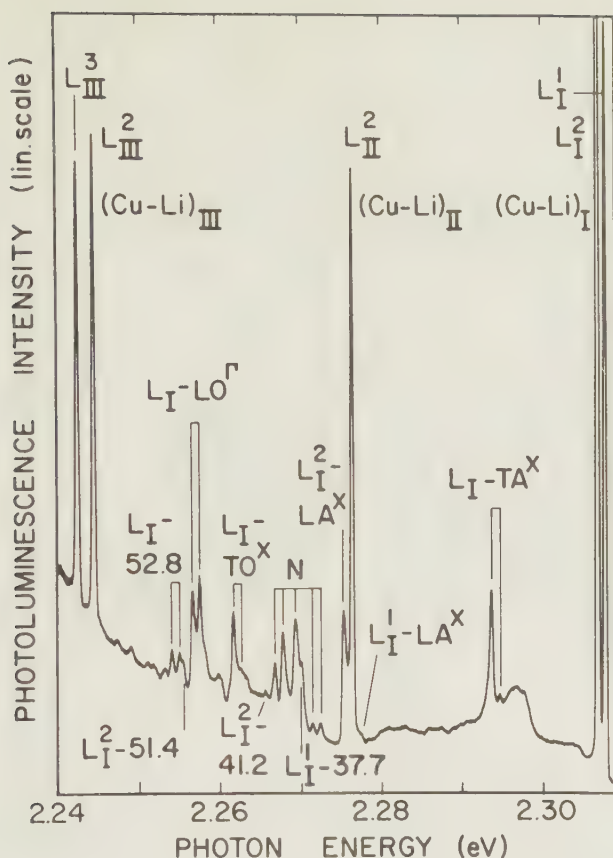


Fig. 2a. Portion of the low temperature (2 K) PL spectrum from a (Cu,Li) doped GaP crystal. At this temperature thermalization favours spin forbidden transitions from the lowest BE states of the $(\text{Cu-Li})_{\text{I}}$, $(\text{Cu-Li})_{\text{II}}$ and $(\text{Cu-Li})_{\text{III}}$ centers. Hence phonon replicas of both L_1 and L_2 are observed in the spectrum. The MC phonons at the X-point of the Brillouin zone show a particularly strong coupling to L_2 , as expected for a forbidden transition. Note that the L_0^{Γ} couples strongly to both components of $(\text{Cu-Li})_{\text{I}}$. A list of electronic lines and phonon replicas is given in Table I.

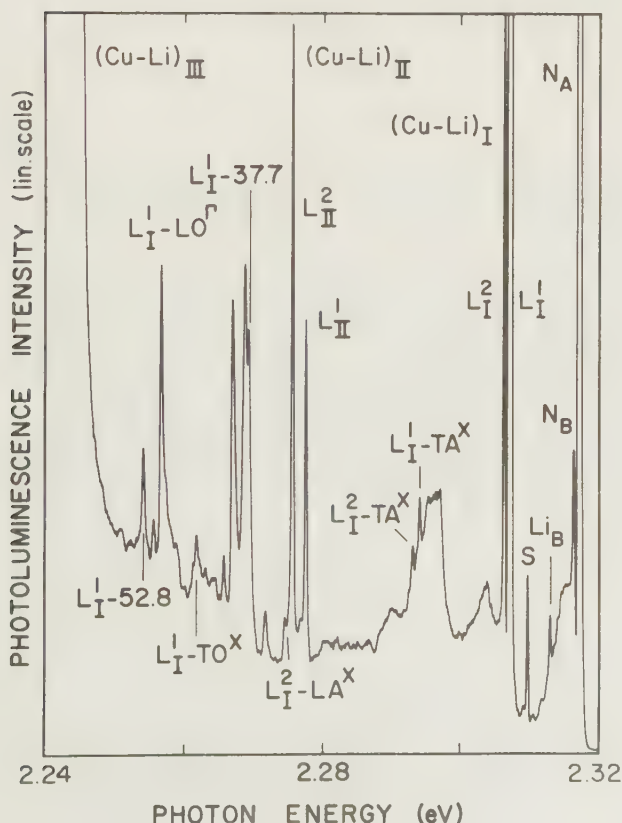


Fig. 2b. Selected part of PL spectrum covering the same energy interval as in Fig. 2a at elevated temperatures (10 K). At this temperature the electronic singlet states are becoming thermally populated. The L_I^I line and its phonon replicas are strong while the L_{II}^I line is weak. The dramatic rise of the $(Cu-Li)_{III}^I$ emission seems remarkable, as shown to the left in the figure. The TAX replicas of both L_I^I lines are observed but the $T0^X$, $L0^I$ and the local 52.8 meV mode replicas are clearly seen only for the L_I^I line.

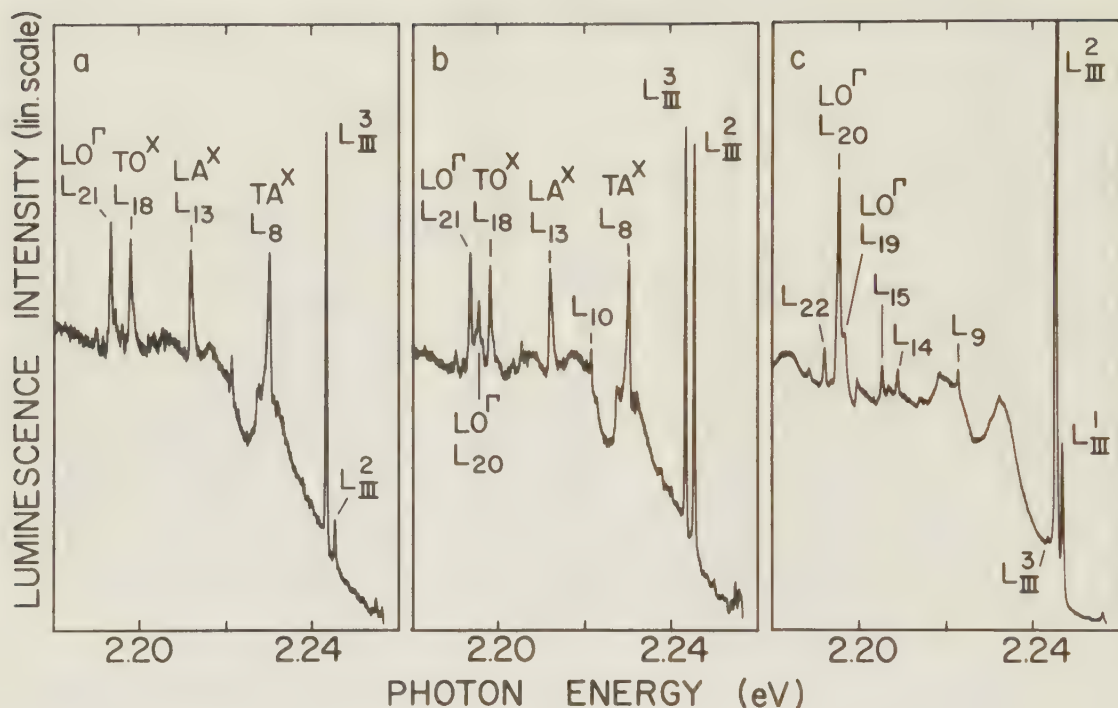


Fig. 3. Portion of the PL spectrum for the dominating $(\text{Cu-Li})_{\text{III}}$ emission showing the spectral development as the temperature is raised. All three curves are measured at liquid Helium temperatures, with different sample heating from the laser excitation.

In a) low temperatures below 2 K favour the forbidden triplet L_{III}^3 . The characteristic coupling to zone boundary phonons TAX , LAX and TOX is clearly illustrated. Also the LO^Γ replica is strong. In b) both components of the triplet-singlet pair are of comparable strength at slightly higher temperatures. Of discrete modes only LO^Γ couples strongly to L_{III}^2 , the absence of the X zone-boundary phonons is clearly manifested. In c) L_{III}^1 appears at higher temperatures (10 K). Only the LO^Γ replica is firmly assigned to this line. The emission is much stronger than in a,b) as obvious from the background. Note that L_{III}^3 has almost vanished together with its characteristic phonon replicas. For notations see Table II.

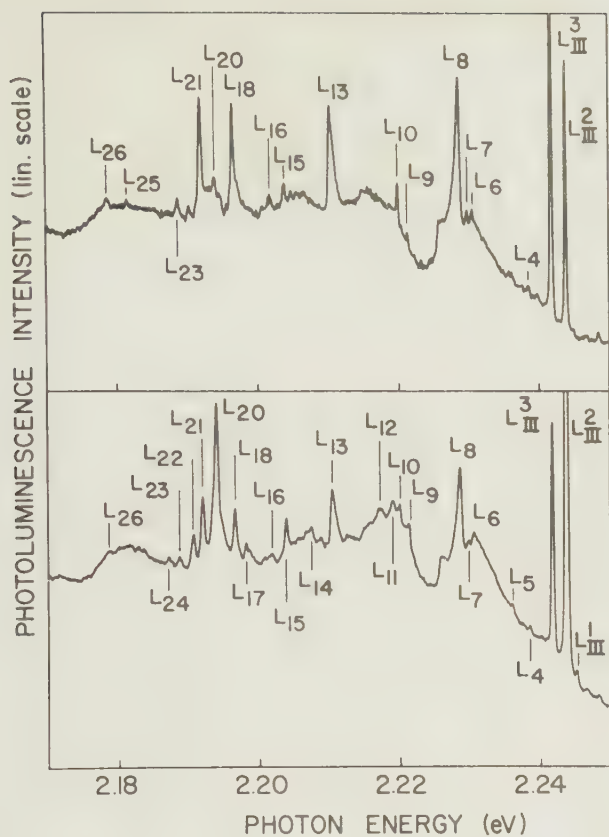


Fig. 4. Selected part of the $(\text{Cu-Li})_{\text{III}}$ emission sideband at slightly different low temperatures (around 2 K). In the upper curve the L_{III}^3 triplet is stronger than the singlet L_{III}^2 , revealing corresponding phonon replicas. $\text{TA}^x(L_8)$, $\text{LA}^x(L_{13})$ and $\text{TO}^x(L_{18})$ are zone boundary phonon replicas of L_{III}^3 . Also $\text{LO}^{\Gamma}(L_{21})$ is strong. L_{16} is a 40.1 meV gap mode and L_{23} , L_{25} and L_{26} are true local modes coupling to L_{III}^3 . In the lower curve the L_{III}^2 singlet is strongest. L_{11} and L_{12} are weak resonance modes, L_{14} and L_{15} gap modes and L_{22} and L_{24} are local modes coupling to L_{III}^2 . The strong L_{20} peak is the LO^{Γ} replica of the singlet line. For a detailed list of phonon replicas see Table II.

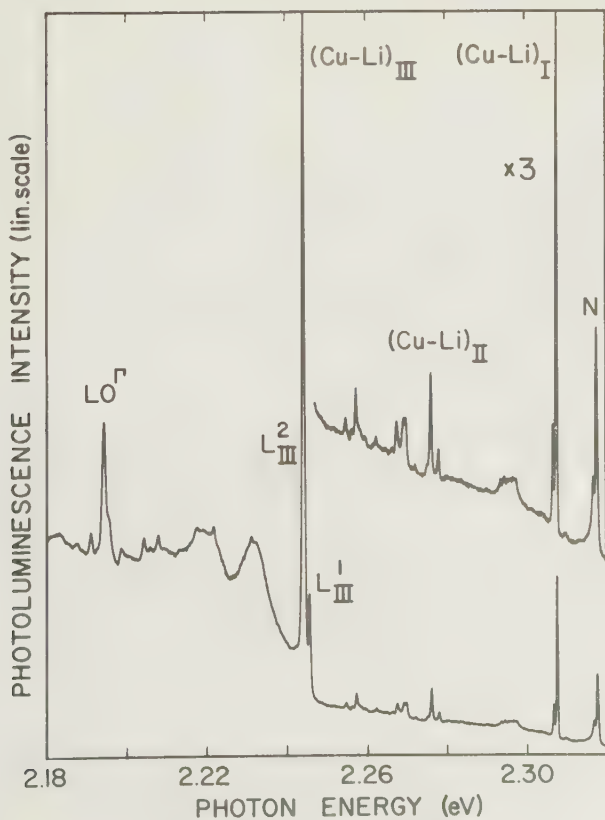


Fig. 5. At higher temperatures (20 K) the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$ emissions are getting thermally quenched. The $(\text{Cu-Li})_{\text{III}}$ emission here totally dominates the spectrum, even after all other structure has vanished. As usually at higher temperatures the L_{III}^2 component is strongest and the phonon sideband consists mainly of continuous acoustic modes coupling to this line (in the one phonon region). For comparison see Fig. 1a which shows completely different relative strength of the (Cu-Li) emissions at low temperatures (2 K).

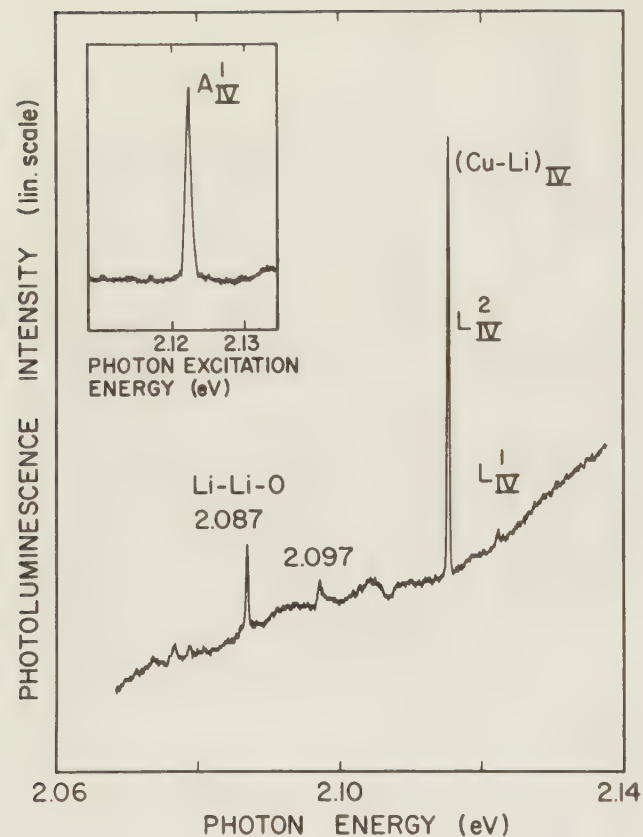


Fig. 6a. Low temperature PL spectrum of the $(\text{Cu-Li})_{\text{IV}}$ emission (2 K). A spin forbidden triplet L_{IV}^2 is strongest, showing weak phonon structure around 2.097 eV. This transition is not observed in PLE spectra. A higher energy component L_{IV}^1 (displaced 7 meV) is very weak in emission due to thermalization, but clearly detected in PLE spectra as shown in inset (A_{IV}^1). This line is probably the singlet corresponding to the L_{IV}^2 triplet BE state. The Li-Li-O bound exciton spectrum at 2.087 eV partly overlaps the $(\text{Cu-Li})_{\text{IV}}$ emission in all crystals.

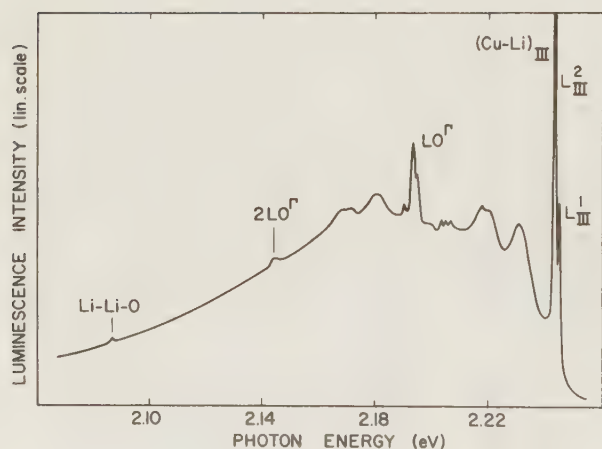


Fig. 6b. Photoluminescence spectrum at elevated temperatures (20 K) showing only the strong $(\text{Cu-Li})_{\text{III}}$ emission after the $(\text{Cu-Li})_{\text{IV}}$ emission is quenched. This is the same situation as for the two higher energy emissions $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{II}}$. The Li-Li-O electronic line is still weakly detectable.

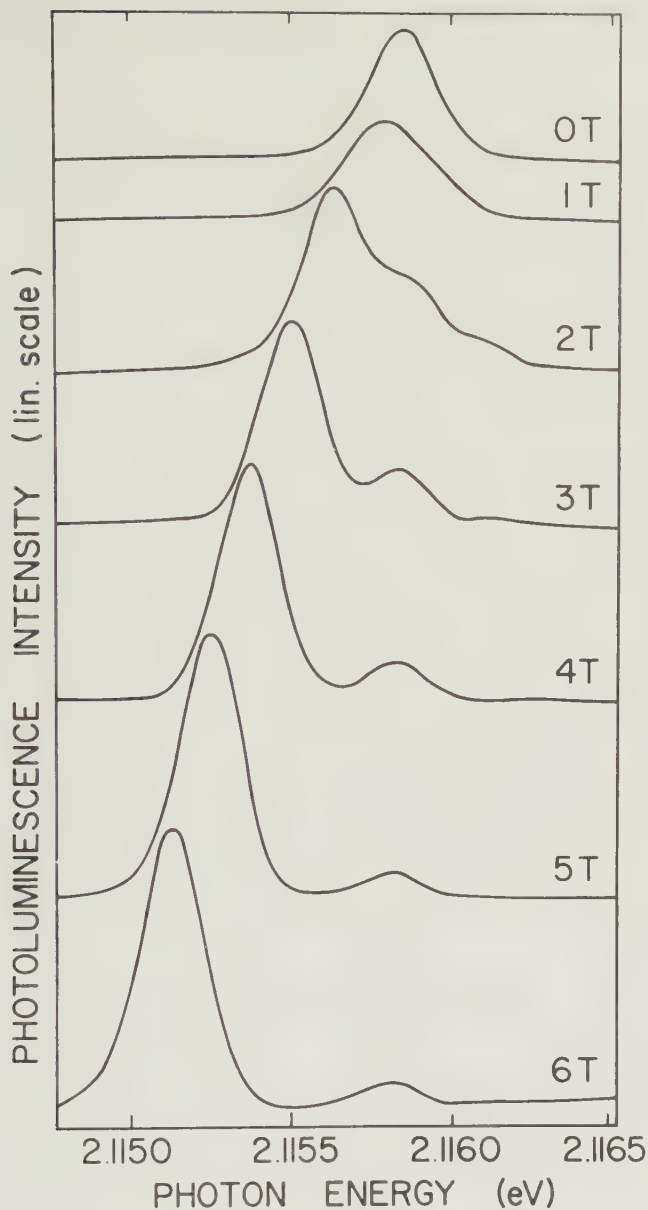


Fig. 6c. A photoluminescence spectrum of the L_{IV}^2 transition at 2.1158 eV in magnetic fields of different strength oriented along the $\langle 111 \rangle$ direction. A symmetric splitting is observed corresponding to an isotropic g value $g \approx 1.95$. The magnetic subcomponents are strongly thermalized favouring the lowest $M_J = -1$ transition, which also gains in oscillator strength compared with the unsplit zero-field line.

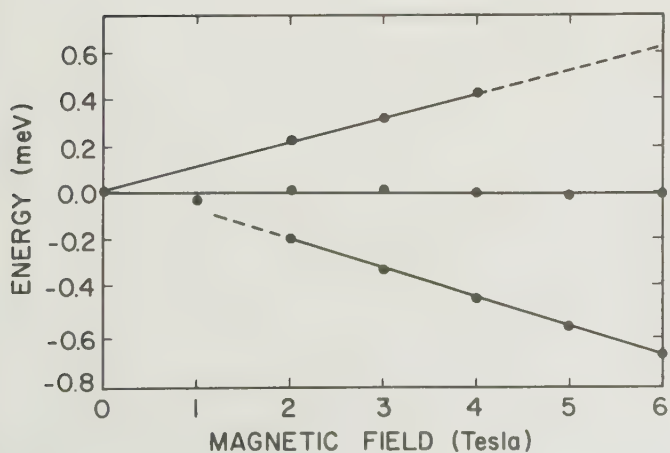


Fig. 6d. A graphical illustration of the experimental curves in Fig. 6c, showing the symmetric splitting of the L_{IV}^2 transition at 2.1158 eV in magnetic field up to 6 T. Magnetic subcomponents which are unresolved or vanish by thermalization are indicated with a broken line.

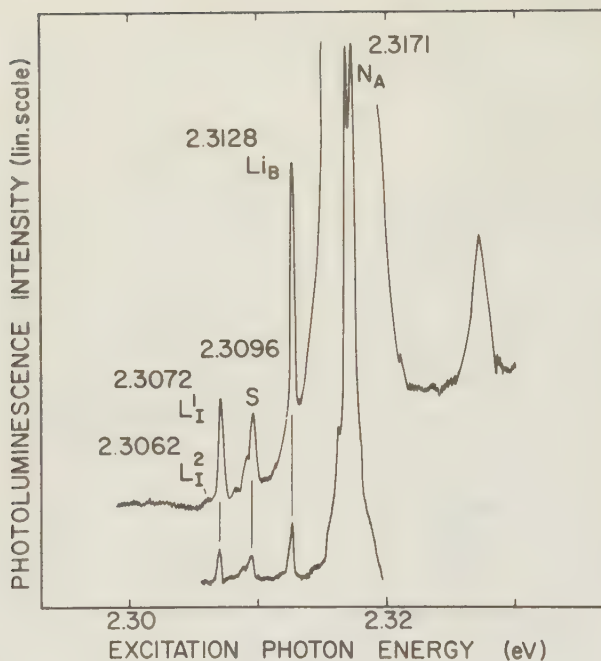


Fig. 7. Low temperature photoluminescence excitation spectrum (PLE) of the $(\text{Cu-Li})_{\text{I}}$ bound exciton spectrum measured with a tuneable dye laser excitation. Detection was made possible through excitation transfer to the $(\text{Cu-Li})_{\text{III}}$ emission. The $(\text{Cu-Li})_{\text{I}}$ emission shows too weak phonon sidebands for a selective detection of this emission. The spin forbidden triplet L_{I}^2 is extremely weak, while the singlet L_{I}^1 is pronounced. Strong peaks due to other well known bound excitons in GaP illustrate excitation transfer to the $(\text{Cu-Li})_{\text{III}}$ emission from these as well. The Li_B exciton at 2.3128 eV is very distinct, also the N exciton is marked. The peak at 2.328 eV is N-related.

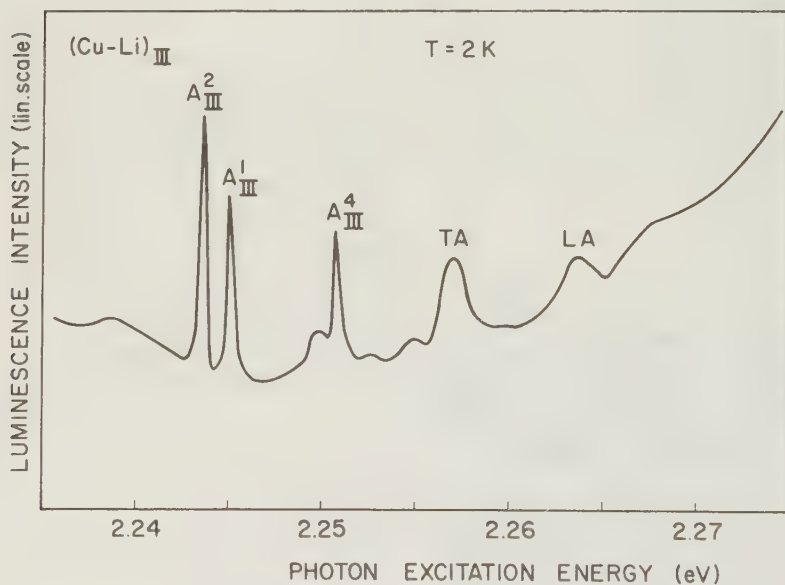


Fig. 8. PLE spectrum measured with a tuneable dye laser excitation at low temperature for the dominant $(\text{Cu-Li})_{\text{III}}$ emission. The detection wavelength was set to 5600 Å. Only faint structure on a strong background is detected, probably due to a rather low concentration of these centers in the material. Two step excitation also is important as obvious from Fig. 7. No signs of the A_{III}^3 (L_{III}^3) triplet at 2.2419 eV are detectable. The A_{III}^2 and A_{III}^1 components (L_{III}^2 and L_{III}^1 in emission) are of comparable strength in absorption. A fourth $(\text{Cu-Li})_{\text{III}}$ electronic line (labelled A_{III}^4) at 2.2509 eV is found in the PLE spectra. This component is split 9 meV from the lowest BE state L_{III}^3 .

Photoluminescence studies of the 1.911 eV Cu-related complex in GaP

H.P. Gislason and B. Monemar

University of Lund, Department of Solid State Physics,
Box 725, S-220 07 Lund 7, Sweden

P.J. Dean and D.C. Herbert

RSRE, St Andrews Rd, Gt Malvern, Worcs, VR14 3PS, England

S. Depinna, B.C. Cavenett and N. Killoran

Department of Physics, University of Hull, HU6 7RX, England

Abstract

The optical properties of the 1.911 bound exciton in Cu-doped GaP have been investigated with several photoluminescence techniques. Photoluminescence- and photoluminescence excitation data at different temperatures are combined with magneto-optical data from Zeeman- and high resolution ODMR measurements. The doping conditions required for this BE spectrum to appear, as well as isotope experiments prove that the defect binding the exciton involves Cu. A neutral and isoelectronic complex is suggested, most probably a linear $(\text{Cu-Ga})_{\text{Ga}}\text{-Cu}_{\text{I}}$ defect with a $\langle 100 \rangle$ -oriented symmetry axis determined from ODMR data. The axial compressional strain field consistent with this defect geometry completely decouples the spin-orbit coupling of the bound hole states, leaving pure spin hole states with lowest energy. The combination of two spin particles accounts for the $J=1$ spin-triplet and $J=0$ singlet states for the bound exciton. The spin forbidden transition from the $J=1$ triplet to the spin-free ($J=0$) ground state is the 1.911 transition dominating the emission spectrum at low temperatures, while

the $J=0$ BE state is observable at 2.002 eV in PLE. The extraordinary large exchange splitting of 91 meV is related to the unusual degree of localisation, since both particles of the exciton are tightly bound. A splitting of hole states in the axial field of the defect is estimated to about 280 meV, exceeding the spin-orbit splitting by at least 200 meV.

I. Introduction

Many impurities and lattice defects are known to cause deep levels in semiconductors, but very few have been positively identified as to their detailed local lattice arrangement [1]. Cu is known to diffuse rapidly into most semiconducting materials at normal processing temperatures and it causes a large number of deep level defects in e.g. Si [2], GaAs [3] and GaP [4]. Some of these are believed to cause severe problems in devices, e.g. degradation of device performance [5]. It seems that the class of defects usually called complexes, i.e. composed of at least two atoms or lattice point defects is very common in semiconductors, favoured by pairing mechanism upon cool-down after growth or heat treatments [6]. Such defects are often neutral and some may be clearly identified as iso-electronic [7], in which an impurity or defect molecule is clearly isoelectronic with the host species replaced. This property makes them accessible to optical studies via photoluminescence techniques [8], even for excitons of large localisation energies. On the other hand it appears to be difficult to study these defects with standard junction space charge techniques, such as DLTS [9], due to low sensitivity [10]. Since defects of this class are often able to capture both electrons and holes, they may be important excess carrier recombination centres, and therefore of great practical interest.

In this paper is reported an optical investigation of a deep Cu-related centre in GaP, binding an exciton which has the lowest electronic excitation energy at 1.911 eV at 2 K. This centre is introduced by diffusion at temperatures 1000 - 1100 °C, followed by rapid quenching to room temperature. Several other bound excitons are observed as a result of such Cu-diffusion, the most prominent being the COL-emission with a lowest electronic line at 2.1774 eV at 2 K [11]. For the 1.911 eV centre it has been possible to carry out a complete optical study to identify the defect and its electronic properties. From a combination of photoluminescence emission spectra (PL) and excitation spectra (PLE) with magneto-optical data from ODMR, a tentative identification of the 1.911 eV defect as a <100>-oriented Cu-Ga associate is suggested but other models are discussed as well. Preliminary results from the ODMR investigations have already been published separately [12]. These results show that the lowest bound exciton state is a nearly pure spin triplet, in agreement with earlier Zeeman measurements [8]. While Zeeman data only showed an isotropic triplet splitting, from ODMR measurements it was also possible to establish the defect orientation firmly. The triplet configuration together with the presence of higher electronic states, split off from the lowest bound exciton state by several tenths of an eV, suggest that both the electron and the hole are fairly strongly bound in the case of the 1.911 eV centre. This situation creates more complicated bound exciton states than the previously studied complexes of NN-pairs [13] or Cd-O and Zn-O pairs in GaP [14,15], where one of the particles (the hole) can be described as bound in a shallow state (about 40 meV) by a Coulomb potential [16]. We believe that the general results obtained here for the electronic structure of these deeply bound Cu-related exciton states are very helpful in the development of a theoretical understanding of deep level complexes in general.

In Sec. II below the procedures for material preparation and doping required to obtain the copper related defects are described. The experimental techniques in the optical measurements are also briefly discussed.

Section III:1 includes photoluminescence data for the 1.911 eV centre at 2 K. At low temperatures a detailed structure due to phonon replicas is observed in the emission. Several of these phonon modes show isotope shifts when Cu^{63} is replaced by Cu^{65} . In Sec. III:2 the spectral evolution at elevated temperatures is shown over a wide temperature range. Also the thermal quenching of PL emission intensity is documented up to 130 K where the emission disappears.

In Sec. IV selective absorption data are presented for the 1.911 eV defect obtained from photoluminescence excitation spectra (PLE) with a cw dye laser. In addition to the lowest bound exciton state several excited configurations are revealed, all of them much stronger than the lowest triplet state. These excited states were only observed in PLE.

Section V contains a full description of the ODMR data for the 1.911 eV centre. This is the first case where a bound exciton could be studied in detail by ODMR in a III-V compound, and very good data are obtained due to the unusually high sensitivity of ODMR in this case.

A specific model for the electronic properties of the centre is presented under the discussion in Sec. VI. The information on the defect symmetry (ODMR) and excited states (PLE) suggests a dominant $\langle 100 \rangle$ -oriented compressive axial field and a large exchange splitting consistent with a greater electron-hole overlap than in previously studied cases of bound excitons in GaP [17].

II. Sample preparation and experimental procedure

The Cu-doped GaP samples used for this investigation were all diffused with Cu at high temperatures. It was found that material doped with Cu during growth from Ga solutions cooled from 1100 °C to 800 °C (without diffusion) did not show strongly the photoluminescence bound exciton spectra reported here. Rather, other broad emissions were then present, which indicates that different Cu defects were preferably created. The diffusion procedure used to create a strong 1.911 eV emission was to evaporate Cu onto a GaP slice (epitaxial or bulk) and use an evacuated ampoule, backfilled with dry N₂ gas and with an equilibrated GaP-Ga melt adjusted to the employed diffusion temperature. Excess Cu was also placed in contact with the melt. Suitable diffusion temperatures were 1000 °C - 1100 °C, the diffusion time was typically 1 hr, and the samples were rapidly quenched to room temperature after the diffusion. It was found that no major difference in the intensity of the 1.911 eV PL emission occurs with doping and similar intensities were found after diffusion into strongly n-type, nominally undoped and Zn-doped p-type wafers. Also the 1.911 eV spectrum could be produced easily in both bulk and LPE GaP material.

For the photoluminescence measurements an Ar⁺ laser, sometimes in combination with a tunable cw dye laser, was employed. Emission spectra and excitation spectra could be recorded from 1.8 K up to 130 K at well regulated temperatures. A double Jarrel-Ash 0.75 grating monochromator was used for obtaining emission spectra, and also on the detection side for dyelaser-excited excitation spectra. Zeeman data of the 1.911 eV line in photoluminescence reported here were obtained at RSRE with a 3.5 T Varian electromagnet. Unfortunately the lifetime broadening of excited states observed in excitation spectra made Zeeman data of these lines impossible

to obtain. ODMR data were obtained at Hull University in an X-band system at 2 K, as described elsewhere [18]. A superconducting magnet was employed and the sample could be rotated in its position inside the rectangular cavity by a gear arrangement, to obtain the angular dependence of the ODMR signal.

III. Experimental results

III:1 Emission spectra

In Fig. 1 is shown the high energy part of the photoluminescence spectrum of Cu-diffused GaP recorded at 1.8 K. The spectrum is dominated by the so called COL emission [11] with a sharp electronic transition at 2.1774 eV. The COL centre has recently been identified as a neutral Cu associate in GaP, and its properties are discussed elsewhere [11,19-22]. On the low energy tail of the COL emission a second Cu-related spectrum is usually present (Fig. 1). Both these transitions are characterized by a very long decay time, at the order of 100 μ s [20,22]. A sharp electronic line at 1.911 eV is characteristic for the low energy emission as shown in more detail in Fig. 2. This line is found to split into a nearly isotropic triplet in a magnetic field (Fig. 2). In addition, a structured phonon side-band is present at lower photon energies with phonon energies as listed in Table I. The most prominent phonon replicas are labelled in Fig. 2 as B_1 at 10.3 meV, B_5 at 24.2 meV and B_9 at 39.9 meV below the no-phonon line. This last mode is a local gap mode, frequently seen in other bound exciton spectra in GaP [11,23,24]. A remarkably low intensity is observed for phonon modes in the optical energy range, between 45 and 50 meV. Thus the $T0_T$ and $L0_T$ replicas are not resolved clearly. At 1.8553 eV, however, or 55.7 meV below the electronic line a sharp peak B_{11} illustrates a weak

phonon coupling to a rather high energy true local mode, that is a phonon mode above the highest phonon energy of the GaP host lattice. Coupling to other true local modes seems absent.

Several of the discrete phonon replicas show a sizeable isotope shift upon substitution of Cu^{63} with Cu^{65} as listed in Table I. Only a very small shift is observed for the electronic line, however. The low energy quasilocalized phonon mode B_1 at 10.3 meV might account for the major part of the phonon sideband through a coupling constant $S \approx 1$. The broad peak at about 22 meV then is the second replica, whereas the third and fourth replicas appear at about 34 and 48 meV, illustrating anharmonic effects in the final vibronic state of the transition. This low energy phonon mode B_1 is also present at elevated temperatures on the anti-Stokes wing. The first anti-Stokes replica is clearly resolved at temperatures above 25 K, showing phonon energies reduced by about 10 % in the excited vibronic state compared with the ground state (Fig. 3). The interpretation of the phonon sideband of the 1.911 eV emission as being mainly composed of multiphonon replicas of a single 10 meV mode with sharper discrete structure superimposed, is even more appealing with rising temperature, when this discrete structure becomes smeared out. At higher temperatures the spectrum can be viewed as consisting only of these broad replicas at about 10 meV intervals, following the no-phonon line.

The different crystals used in this investigation often show weaker sharp lines 9.2 meV, 23 meV and 38 meV above the 1.911 eV electronic line. Occasionally these extra emission lines are absent, and their intensities do not correlate with the 1.911 eV emission. Consequently these lines are not related to the 1.911 eV emission, but rather to an independent emission from an unknown centre. To illustrate this situation the spectrum of a crystal different from the one used in Fig. 2 is shown in Fig. 4. Here the line at 1.9202 eV is about half as strong as the 1.911 line when

excited with above bandgap excitation (5145 Å). When excited in the strong 2.002 eV absorption line obtained selectively for the 1.911 eV emission in PLE measurements (see below Sec. IV), the 1.9202 eV line does not show a resonant enhancement of the intensity as the 1.911 eV line does. The 1.911 eV line now dominates over the higher one and its characteristic phonon sideband is revealed. This procedure proves that the lines in fact belong to different centres.

III:2 Temperature dependence of the 1.911 eV emission

As already mentioned, the phonon coupling of the 1.911 eV electronic line is dominated by coupling to a single quasilocalized mode of about 10 meV, giving the structured emission spectrum shown in Fig. 2 at low temperatures. The coupling strength for this emission is rather weak. The Huang-Rhys factor S , evaluated from the ratio between the integrated intensities of the zero-phonon line and the total emission according to the equation $I_0/I = \exp(-S)$ [25] gives $S \approx 2$. This is considerably smaller than in the case of the COL emission where $S \approx 5$ [19] (cf. Fig. 1).

The electronic line of the 1.911 eV emission is clearly visible as a discrete peak up to about 80 K, although drastically smeared out as shown in Fig. 5. About 80 K the no-phonon line can still be easily distinguished as a broad shoulder at photon energies between the increasing anti-Stokes wing and the envelope showing faintly the broad 10 meV phonon replicas. At 100 K this structure disappears together with the no-phonon line, leaving a smooth emission envelope. In contrast to the COL which shows a strong coupling to low energy modes, both discrete and continuous, this behaviour is typical for a rather weak coupling to the continuous acoustic phonon bands and the absence of any strong low energy discrete modes. Consequently the no-phonon line vanishes in the COL emission at much lower temperature or just above 40 K [19].

A marked increase in the background intensity is observed at temperatures above 100 K, where the remaining intensity of the 1.911 eV emission appears superimposed on a broad emission extending from about 6200 Å down to beyond 7000 Å, with its maximum around 6500 Å. This background was subtracted when evaluating the curve in Fig. 6, which shows the temperature dependence of the total emission intensity for the 1.911 eV emission. Only a slight decrease of the intensity (within 15-20 %) is observed in the low temperature region up to about 80 K. This decrease may be partly overvalued due to difficulties in separating the electronic quenching for such a structured emission from vibrational broadening effects, which conserve the area under the emission curve. The thermal activation energy observed as the emission envelope rapidly disappears in the temperature range 100-130 K is $E_1 = 120 \pm 10$ meV for extrinsic excitation at 2.03 eV. A second smaller activation energy $E_2 = 30 \pm 5$ meV is deduced from the slope of the gradually decreasing intensity curve before the final step. The overall shape of the quenching curve is described by the expression

$$I(T) = I(0) [1 + C_1 \exp(-\frac{E_1}{kT}) + C_2 \exp(-\frac{E_2}{kT})]^{-1}$$

where the weight factors $C_1 = 4 \cdot 10^5$, $C_2 = 25$ express the relative importance of each step. Measurements with intrinsic excitation at 5145 Å give qualitatively similar results; the discrete structure disappears around 100 K and the emission is undetectable above 130 K. A marked difference though, is a considerably lower activation energy ($E = 50 \pm 5$ meV) than for extrinsic excitation. The curve is described by this slope alone. Consequently the decrease is more rapid at lower temperatures than in the extrinsic case, but slower towards higher temperatures. This difference is very probably due to other effects than thermal release of particles from the 1.911 eV centre [13].

IV. Photoluminescence excitation spectra

In Fig. 7 is shown the low temperature PLE spectrum of the 1.911 eV emission, obtained with a cw dye laser in the energy range between 1.9 eV and the bandgap. The detection monochromator wavelength is selectively set to portions of the emission envelope, alternatively to 6550 Å and 6650 Å to exclude possible interference with Raman scattering lines. The excitation spectrum consists of a weak electronic line at 1.911 eV, corresponding to the emission line at the same energy. This line has a surprisingly low oscillator strength and is indeed very difficult to detect even with dye laser excitation. Therefore no clear signs of the structured phonon wing present in emission are seen in the absorption spectrum. However, at 1.956 eV a group of weak and badly resolved lines is seen, the strongest one being a factor of 10-15 stronger than the 1.911 eV triplet. This peak has a linewidth of approximately 1.5 meV, which indicates that it is a lifetime broadened excited state. A careful inspection of PLE curves for different crystals shows that this broad feature is connected with a weaker sharp line at 1.949 eV, which is also sometimes seen in emission, although barely detectable. We therefore conclude that these features are not related to the 1.911 eV centre, and their appearance in the PLE-spectrum is due to a different defect.

At 2.002 eV a strong and broad line A_0 (half-width 2 meV) marks the edge of a richly structured absorption wing extending up to the band edge region. From the previous discussion it is clear that this strong wing originates from the 1.911 eV emission. When exciting in the 2.002 eV line the 1.911 eV emission is selectively enhanced, and in addition the absorption wing occurs only when detecting this emission. From Fig. 7a it is evident that almost the total oscillator strength of the optical transitions related to this bound exciton lies in the higher energy components

starting at 2.002 eV. The relative intensities of the 1.911 eV B_0 line and the strong 2.002 eV component A_0 is about 1:100, and even lower when the phonon assisted sidebands are taken into account. The discrete phonon structure connected with the A_0 transition resembles closely the corresponding phonon wing of the 1.911 eV line in emission. This is another strong argument for the identification of the 2.002 eV line as an excited configuration of the bound exciton having its lowest state at 1.911 eV. In Table II the phonon energies from the excitation measurements are listed, the notation referring to the labels in Fig. 3.

The sharp peak at 3.8 meV above the A_0 electronic line does not correspond to any phonon mode in emission. Otherwise the structure largely consists of a strong coupling to a 10 meV phonon mode in a similar way as for the 1.911 eV emission line B_0 . The first replica A_1 , 10.2 meV above A_0 is strongest, while the second one, 21 meV above the A_0 line, is still very distinct. The third replica (33 meV) is merging into the continuum background and partly hidden by the sharp peak A_8 , 34.8 meV above A_0 . A_8 is not represented in the emission spectrum. However, the 37.4 meV B_8 mode is fairly close to the A_8 mode in energy, being a localized gap mode as well. The energy difference is 2.6 meV between the A_8 and B_8 modes while the A_9 mode of 38.7 meV is 1.2 meV lower in energy than the strong B_9 gap mode of 39.9 meV. On both sides of this mode dips occur in the excitation spectrum in a similar manner as for the emission spectrum. The high energy shoulder of the dip lies at 42.5 meV which is also the value for the corresponding feature in emission. This is close to the lower edge of the optical density-of-states branch for pure GaP lattice [26].

No major discrete peaks occur in the absorption spectrum above 2.10 eV until a strong broadened (half-width about 1 meV) electronic line C_0 appears at 2.1928 eV, more than 0.28 eV above the 1.911 eV ground state

(Fig. 7b). Above this line a well resolved structure has the proper width and energy range to represent phonon replicas of the C_0 line. This excitation structure appears only when the detection wavelength is within the 1.911 eV emission band, which associates it with this Cu-centre. The strongest peaks are C_1 , a rather broad (2 meV) peak 16.8 meV above C_0 , closely followed by another much weaker one, 4 meV higher in energy. A pair of peaks C_2 and C_3 at 34 meV and 37.2 meV above C_0 are relatively sharp as expected for localized gap modes, and are therefore most likely phonon replicas of the C_0 electronic line. No further structure is found in the absorption spectrum up to the nitrogen bound exciton line, N_0 , which occurs as a narrow dip in the spectrum. This is in contrast to the COL emission in the same crystals (Fig. 1) which gets a considerable excitation transfer at the N_0 bound exciton energy [11]. No other well known shallow exciton lines are observed in this excitation spectrum. It is also interesting to note that excitation transfer from the dominating COL spectrum (Fig. 1) in these crystals is apparently very weak and not observed in Fig. 7. This can be understood in terms of a rather small concentration (probably $< 10^{16} \text{ cm}^{-3}$) for both the COL centre and the 1.911 eV centre discussed here, and the large binding energy E_{BX} of the COL. Radiation-field transfer will also be poor because of low oscillator strengths.

V. ODMR results

The experimental technique used in obtaining ODMR data was briefly discussed above under Sec. II. All data discussed here were obtained with the sample immersed in pumped He at 2 K and at X-band ($\sim 9\text{GHz}$) microwave frequencies. For the 1.911 eV emission an unusually strong ODMR signal was observed, since the fraction of the total PL signal that was modulated

with the microwave field was as high as 5 %. This is fortunate since it makes very detailed and well resolved resonances obtainable. A preliminary report has been published [12]. An example of typical ODMR signals for the orientation $\bar{k} // \bar{B} // [001]$ is shown in Fig. 9, where resonances in both the circularly polarized emission components $\Delta I_{\sigma+}$ (upper) and $\Delta I_{\sigma-}$ (lower) are shown. Both signals are in fact increases in emission intensity, which means that the total emission intensity is also increased by the microwave field. This is the usual case when we have an unthermalized or a partly thermalized triplet system, i.e. the emission lifetime τ is shorter than the spin relaxation time T [18].

The ODMR signal of Fig. 9 was obtained by monitoring a broad spectral range of the emission, with an edge filter cutting out light at wavelengths shorter than 6600 Å to obtain optimum signal-to-noise ratio for a detailed analysis of the resonance shapes. To ascertain that the ODMR signal was actually derived from the 1.911 eV triplet emission, the spectral dependence of the ODMR intensity was measured. In this case a fixed magnetic field was employed and the spectrum of ΔI was obtained by using a monochromator in front of the photomultiplier. As shown in Fig. 10 the spectrum of the microwave-induced PL signal at resonance is exactly the same as the 1.911 eV PL emission (Fig. 2). It can be seen that the tail from the COL emission (Fig. 1) does not contribute to the ODMR signal, confirming that this signal is only related to the 1.911 eV PL spectrum. It should be noted that the detailed structure obtained in the spectral dependence measurement allows independent confirmation of the assignment of the phonon replicas to the 1.911 eV system.

The expected level crossing phenomenon for a triplet exciton state, i.e. the change in PL intensity upon variation of the magnetic field with no microwave field applied, could also be observed, as evident from Fig. 11.

As shown below in Fig. 12 the states $|-\rangle$ and $|0\rangle$ cross for a certain value of the magnetic field $\bar{B}/\bar{Z}$, in which case a mixing between these states occurs. This mixing allows the $|0\rangle$ state to emit light, giving rise to a total increase in the emission intensity (Fig. 11). This provides an independent identification for the observation of an uncompletely thermalized triplet system [18]. We see no evidence of a hyperfine structure analogous to that observed by Lee et al. [27] in this case. In Fig. 9 is noted the observation of pairs of resonances for each axial centre with different orientation relative the $\bar{Z} \equiv [001]$ axis of the experiment, which is characteristic for a triplet exciton. The Hamiltonian describing these bound exciton states in a magnetic field $\bar{B}$ is [18]

$$H = \mu_B \cdot \bar{B} \cdot \bar{g}^{\text{ex}} \cdot \bar{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + E[S_x^2 - S_y^2] \quad (1)$$

For an axial centre (where E is small) the basis states are $|+1\rangle$, $|0\rangle$ and $|-1\rangle$, and the zero field splitting between $|\pm 1\rangle$ and $|0\rangle$ states is determined by the parameter D . If an orthorhombic distortion is present as in this case, the last term in Eq. 1 has to be included. Then the two $|\pm 1\rangle$ states are also split in zero magnetic field and labelled $|\pm\rangle$. The three principal directions describing the $[001]$ defect are $\bar{x} \equiv [110]$, $\bar{y} \equiv [1\bar{1}0]$ and $\bar{z} \equiv [001]$ and the corresponding energy level schemes for the magnetic field parallel to these directions are shown in Fig. 12. If the system is unthermalized the population differences between these energy levels are determined by the different decay rates from the levels. Thus the levels with high emission rates empty preferentially and at resonance the micro-waves induce transitions to these states from weakly emitting states. A similar situation occurs for partly thermalized systems. This is also illustrated in Fig. 12, where for the magnetic field along the major axis ($\bar{Z}$) of a defect the $|0\rangle$ state emission is weak. Two resonances are observed,

as shown, $|0\rangle \rightarrow |+\rangle$ which increases the $I_{\sigma+}$ emission principally at low field and $|0\rangle \rightarrow |-\rangle$ which increases the $I_{\sigma-}$ emission at high field. These resonances are separated by $\frac{2D}{g^{\text{ex}}\mu_B}$ and the mean field position gives g^{ex} .

The ODMR spectrum for GaP:Cu is more complicated than that observed in an axial crystal such as GaSe [28] since it is clear that there will be a set of three axial defects for symmetry $\langle 001 \rangle$. For orthorhombic centres there will be six inequivalent defects and since each exciton gives two triplet resonances a total of 12 ODMR signals may be observed for an arbitrary angle between the magnetic field and the crystal axes. In the present case the ODMR spectrum for $\bar{B}/[001]$ can be seen to contain two distinct pairs of lines and as labelled on the diagram these correspond to the three $\langle 100 \rangle$ centres; $[001]/\bar{B}$, $[010] \perp \bar{B}$ and $[100] \perp \bar{B}$. The separation between the resonances is determined by the angles between the axes of the centre and the magnetic field direction. Observations of the ODMR spectra as $\bar{B}$ was rotated in the (110) and (100) planes of the crystal confirmed that the resonances are due to $\langle 001 \rangle$ centres. The results for rotation in the (110) plane are shown in Fig. 13a, where the solid lines have been calculated using the Hamiltonian in Eq. 1. Fig. 13b shows the angular dependence for rotation in the (001) plane and a fit using Eq. 1. The corresponding spin Hamiltonian parameters were found to be $g_x = 2.20 \pm 0.01$, $g_y = 1.95 \pm 0.01$ and $g = 2.05 \pm 0.01$, further $D = 0.013 \pm 0.001$ meV and $|E| = 0.0025 \pm 0.0006$ meV.

It is apparent in Fig. 13 that there is a low field transition which shows only slight anisotropy. This is, in fact, the $\Delta M_S = \pm 2$ transition which is shown on the energy level diagram (Fig. 12). The position of this line depends principally on the g-value and since this is nearly isotropic, $g \approx 2$, the $\Delta M_S = \pm 2$ transition occurs near an effective $g = 4$. For $\bar{B}/[001]$ this transition is very weak for the usual experimental arrangement (the

oscillating rf field perpendicular to the z axis of the system) though it can be seen in Fig. 9. However, the intensity of this line increases as $\bar{B}$ is rotated away from the defect axis. This is obvious from Fig. 14 where an ODMR spectrum is shown for $\bar{B} // [110]$. For $\bar{B}$ away from the z-direction the emission is allowed for each level so that population differences are small and all resonances are weak (Fig. 14). A small degree of thermalization and different decay rates from the $|+\rangle$ and $|-\rangle$ states account for the observation of the $\Delta M_S = \pm 2$ transition. Also, the sign of the D as positive is clear from the effect of thermalization on the magnitude of the ODMR signals (for $\bar{B} // [001]$, $\Delta I_{\sigma+} > \Delta I_{\sigma-}$).

VI. Discussion

The new information on the 1.911 eV centre in GaP:Cu obtained in the present study illustrates the complexity of such deeply bound exciton systems, which do not seem to correspond to previously studied deep BE states in GaP, (e.g. Zn,0 and Cd,0 [14,15]). The theory for bound exciton states available in the literature is not directly applicable to the detailed electronic structure of the complex Cu-defects responsible for the COL emission [11] and the 1.911 eV emission. We have therefore developed a tentative model for the observed electronic structure of the 1.911 eV centre based on the new information on the identity of this defect.

Before discussing our models for the identity and electronic structure of the 1.911 eV centre, a short summary of the relevant experimental data available seems justified. The photoluminescence data in connection with the doping conditions give the information that Cu is involved, and that the electronic triplet observed at 1.911 eV is in agreement with an exciton bound to an isoelectronic centre. Attempts to prove possible

association of Cu with other impurities have shown no connection with intentional or inadvertant dopants such as S, Te, O, N, S or Zn. Further, isotope shifts are observed in the sharp phonon replicas of the 1.911 eV sideband when $\text{Cu}^{63} \rightarrow \text{Cu}^{65}$ (Table I). These shifts are as large as 0.5 meV in the 24 meV replica, which is probably a locally perturbed LA mode. The presence of Cu in the complex is thus proved and since the LA_χ mode involves the motion of the Ga sublattice only [29] the selectively largest isotope shift for a perturbed such mode indicates a Cu_{Ga} substitute [30]. The Zeeman measurements of the 1.911 eV line show an almost symmetric splitting into three components in magnetic field (Fig. 2) and a nearly isotropic g value, $g \approx 2$, is deduced from the angular dependence of the splitting. Partial thermalization of these three components in a magnetic field up to 6 T proves that the splitting occurs in the initial state of the luminescence transition, ruling out e.g. a transition of an outer electron into a d-shell triplet of the Cu-atom. An important complementary information is provided by the ODMR data, which show the $\langle 100 \rangle$ -orientation of the symmetry axis. This illustrates the higher resolution of the ODMR measurements when the Zeeman analysis is unable to determine the symmetry of the centre.

The data discussed so far provide only results for the lowest state of the bound exciton, being based on low temperature photoluminescence emission spectra. The temperature dependence of the emission intensity adds information on thermal activation energies of the particles involved in the transition. However, in this case the higher bound exciton states are separated too far in energy from the lowest state to become thermally populated before the emission is quenched. Photoluminescence excitation spectroscopy on the other hand provides valuable results for the higher electronic states of the bound exciton. The linewidth of the transitions

to these higher energy states shown in Fig. 7 is lifetime broadened by transitions to lower energy states. A very strong magnetic field would be needed to reveal the multiplicity of these high-energy components. However, by analogy with the COL centre [11] these may well be predominantly due to magnetic singlet exciton states as discussed below.

A model of the defect complex causing the 1.911 eV emission has to account for all the above mentioned pieces of information. The model should include the local arrangement of Cu atoms in the centre, as well as the electronic structure of the exciton bound at the centre.

VI:1. The identity of the 1.911 eV centre

The detailed isotope and doping studies made in this investigation, and also by Wight et al. [22], imply that the 1.911 eV centre involves Cu without correlation to other intentional dopants. However, native defects can neither be revealed by isotope measurements nor doping studies and must therefore be considered as possibly involved in the defect. Cu has the electronic configuration $3d^{10}4s$ and is therefore lacking two valence electrons to complete the local bonds to the phosphorus neighbours when replacing Ga ($3d^{10}4s^24p$). Also Cu can act as an interstitial donor Cu^+ ($3d^{10}$) + e^- ($4s$).

Hence, if a complex is to be neutral and only consist of Cu-atoms with complete d-shells it has to involve three atoms. This is the case for the COL centre, where a $Cu_I-Cu_{Ga}-Cu_I$ defect was found to correspond to the observed properties of that centre [11]. All three Cu-atoms then have the $3d^{10}$ configuration and the substitute is neutral and isoelectronic in the sense that all valence bond requirements are fulfilled in the neutral charge state. Further, the neutral centre has no unpaired electronic spin, and all inner shells are complete.

Accordingly a $\text{Cu}_{\text{Ga}}\text{-Cu}_{\text{I}}$ pair defect where the bands to the neighbouring P-atoms are complete must either accept an electron if both Cu-atoms are to be in the $3d^{10}$ configuration (a charged centre), or the centre has an unfilled d-shell ($3d^9$). In the latter case the centre is neutral and can in principle be viewed as a neutral acceptor, since it is negatively charged upon electron capture. The unfilled d-shell implies that the $\text{Cu}_{\text{Ga}}\text{-Cu}_{\text{I}}$ centre has a magnetic momentum and the ground state of the neutral centre will not be a $J=0$ state as required for an isoelectronic centre. It is possible, though, that the overlap between the d^9 hole and the electronic particles in the BE is sufficiently small to give negligible magnetic coupling, so that the d^9 hole remains unaltered during the BE recombination. This could in fact also be consistent with weak overlap between the d^9 hole and the valence band to give a weak Auger process. Usually strong Auger effects are expected upon the recombination of a tightly bound exciton at a centre binding more than two electronic particles [31]. The very long decay time observed for the 1.911 eV emission is in contradiction to the possibility of such effects. A negatively charged $\text{Cu}_{\text{I}}\text{-Cu}_{\text{Ga}}$ centre where the d-shell is filled could on the other hand account for the electronic properties of the 1.911 eV associate, provided that the material is n-type. Our doping experiments (see Sec. II) however, show that the 1.911 eV centre is equivalently produced in n-type, p-type and nominally undoped material, ruling out this possibility. In addition, excitons bound to charged centres have not been observed in GaP [17].

As shown in Fig. 15 there are two different types of interstitial positions in the zincblende lattice, the tetrahedral (T) and the hexagonal (H) sites [32]. There are two distinct tetrahedral sites along the $\langle 111 \rangle$ axis in e.g. GaP, one surrounded by four Ga atoms, the other by four P atoms (one tetrahedral site T is shown in Fig. 15). The latter is also

situated on a $\langle 100 \rangle$ -oriented symmetry axis relative to a neighbouring Ga site. The midpoint of the two tetrahedral sites is the hexagonal interstitial site H, surrounded by a broken six-membered ring with three atoms of each kind. Relative to a nearest neighbour substitutional site the orientation is approximately $\langle 100 \rangle$. Interstitial atoms can also undergo bonding with the lattice and bond centred interstitials along the $\langle 111 \rangle$ axes are expected in the zincblende lattice as in the diamond lattice [32].

In the diamond structure a pair of two atoms sharing a substitutional site in a bonded configuration in the $\langle 100 \rangle$ orientation is referred to as a split- $\langle 100 \rangle$ interstitial (Fig. 15). All bonds to the four neighbours are complete as well as the bond between the two atoms in question, but each atom in the pair has only three chemical bonds. Six valence electrons are needed to fulfil the bonding requirements, therefore two Si^+ atoms can form a split- $\langle 100 \rangle$ interstitial [32].

A split interstitial pair may result if a Ga atom is not completely released from its lattice position when Cu is introduced. Then both atoms instead share the substitutional Ga site, oriented along a $\langle 111 \rangle$ axis. Such a $(\text{Cu-Ga})_{\text{Ga}}$ defect is neutral only in a d^9 configuration, if the bonds to the neighbouring phosphorus atoms and between the Cu and Ga atoms are complete. Alternatively the split interstitial pair could act as the acceptor part of a molecular isoelectronic centre, where a Cu_I would be the donor. The $(\text{Cu-Ga})_{\text{Ga}}$ split interstitial has the proper defect symmetry axis for the 1.911 eV centre ($\langle 100 \rangle$) and the Cu_I donor must also be situated along this direction. The corresponding interstitial position is a tetrahedral site surrounded by four P atoms. A Cu_I atom at a hexagonal site is, however, approximately $\langle 100 \rangle$ -oriented relative to the Ga site. The same interstitial positions are possible for the case of a $\text{Cu}_I\text{-Cu}_{\text{Ga}}$ pair, although a $\langle 111 \rangle$ orientation seems more natural for the defect symmetry axis of that defect. A $(\text{Cu-Cu})_{\text{Ga}}$ split interstitial pair is far from

satisfying local bond requirements, with only two valence electrons and would require a major rearrangement of the bonds to be realized.

To summarize, there are three lattice configurations considered as models for the identity of the 1.911 eV centre. A pair of two Cu-atoms ($\text{Cu}_{\text{Ga}}\text{-Cu}_{\text{I}}$) and the split interstitial pair $(\text{Cu-Ga})_{\text{Ga}}$ are both consistent with the observed $\langle 100 \rangle$ -oriented defect symmetry axis. If neutral, these centres involve an unfilled d-shell and it must be postulated that the d-hole does not severely interfere with the particles of the bound exciton. The d-hole must be magnetically inactive in the BE transition if the defect is to act as a spin free isoelectronic centre, and Auger effects will have to be negligible due to small overlap of the electronic wavefunctions. Also, the fact that the shallow doping giving both n- and p-type material does not affect the intensity of the BE transition seems to contradict an open d-shell configuration. A third model for the identity of the centre involves a $(\text{Cu-Ga})_{\text{Ga}}$ split interstitial acceptor and an interstitial donor, preferentially Cu_{I} in view of the high concentration of these at the actual diffusion temperature. A neutral isoelectronic centre is formed by analogy with e.g. the molecular centre Zn-O in GaP [14,15]. Here all atoms are postulated to have filled d-shells, eliminating the possibility of Auger effects and the interaction with d-electrons. Also, the defect symmetry axis is in agreement with ODMR results, provided that the Cu_{I} occupies a tetrahedral interstitial site in the P-sublattice.

Additionally, the considerable differences in phonon coupling between the COL Cu-complex and the 1.911 eV complex will also have to be understood in terms of the model for the defect identity. It has been suggested that the complicated low energy mode structure observed for the COL emission as discrete replicas at 5.3, 6.8 and 8.8 meV from the electronic line [11,19] is due to vibrations of the two interstitial Cu atoms. The 10.3 meV B_1 mode of the 1.911 eV emission does not seem to be comparable to these low

energy COL-modes, since it shows no Cu isotope shift (Table I). Compared with the COL the B_1 mode lies in an energy region in which coupling to much higher density of states of lattice modes may dilute the fractional kinetic energy of the Cu ions sufficiently to make the isotope shift hard to measure. If this is not the case the B_1 mode in fact does not involve, the motion of Cu and the model with Cu atoms only has to be rejected.

On balance the models including a native defect (a Ga_I) seem to give better agreement with the observed properties of the 1.911 eV centre. Our tentative conclusion from the above discussion is that a molecular defect consisting of a $(Cu-Ga)_{Ga}$ split interstitial pair and an adjacent Cu_I donor along the $\langle 100 \rangle$ direction is the most natural choice in view of all available experimental data.

VI:2. The electronic structure of the 1.911 eV bound exciton

From the Zeeman and ODMR data displayed in the previous sections it was concluded that the electronic structure of the 1.911 eV bound exciton depends on the axial symmetry of the centre binding the exciton. The final state in the transition is the ground state of a neutral isoelectronic centre having no spin, while the initial state of the bound exciton in emission is found to be a near spin triplet giving an almost isotropic g-value, $g \approx 2$. Similar behaviour has been reported for several other centres [17,33,34] where the isotropic behaviour has failed to reveal the symmetry axis in absence of ODMR data.

In a general model for the bound exciton states these can be regarded as formed from electron states derived from the six $\langle 100 \rangle$ conduction band minima and hole states derived from the uppermost valence band maximum at Γ in the reduced Brillouin zone. The valley-orbit splitting of the six-fold degenerate linear combination of conduction band states, induced by the

localization of the electron, results in a lowest lying Γ_6 (D_{2d} double group) bound electron state with $m_j = \pm 1/2$. The bound hole states can be considered to be formed from p-like orbital states coupled with spin. The D_{2d} ($\langle 001 \rangle$ oriented) axial crystal field splits the p-states into a p_0 ($m_l = 0$) and a $p_{\pm}$ ($m_l = \pm 1$) state, which when coupled with spin form $m_j = \pm 1/2$ (Γ_6) and $m_j = \pm 1/2, \pm 3/2$ (Γ_6', Γ_7) bound hole states respectively. In the limit of a strong axial field the spin-orbit coupling between the Γ_6 and Γ_6' states is quenched and the Γ_6 state tends to behave as a pure spin state. In the case of the 1.911 eV system we have observed magneto-optical behaviour which is consistent with the lowest energy state of the bound exciton being the triplet state (effective spin, $J=S=1$) formed from the Γ_6 bound hole and electron states coupled by the Coulombic exchange interaction, thus:

$$\Gamma_6 \times \Gamma_6 = \Gamma_1 + \Gamma_2 + \Gamma_5$$

The Γ_1 state refers to a $S=0$ singlet BE state and the $S=1$ triplet consists of a Γ_5 ($M_S = \pm 1$) doublet and a Γ_2 ($M_S = 0$) singlet as shown in Fig. 12. The zero field splitting of the $S=1$ triplet state ($D=0.014$ meV) confirms the almost pure spin character of the bound particles [17].

The splitting of the hole states, as discussed above, giving a lowest lying Γ_6 bound hole state implies that the system experiences a strong compressional axial crystal field (as shown in Fig. 16). The sign of the axial field is opposite to the sign appropriate for e.g. the Cd-0 system in GaP [14,15], due to the large ionic radii of the Cu_I atoms. The spin-orbit splitting Δ_{SO} of the GaP host is around 82 meV, whereas the axial field causes splitting of the order of 280 meV as shown in Fig. 16. Mixing of the hole wave function with the 3d states of Cu, which show inverted spin-orbit splitting, might reduce the spin-orbit splitting of the bound hole states, or even result in a negative value compared to the GaP host [35].

In any case the large axial field splitting dominates over the spin-orbit splitting as illustrated in the coupling scheme of Fig. 16.

Comparing the level diagram in Fig. 16 with the experimental data in Figs. 2 and 8 the transition from the $J=1$ bound exciton state (i.e. the effective spin $S=1$) to the ground state singlet refers to the 1.911 eV electronic line seen in emission. This transition has a very low oscillator strength in excitation measurements, illustrating a spin selection rule $\Delta S=0$, according to which the transition is forbidden. The strong line at 2.002 eV observed in PLE spectra corresponds to a transition between the ground state and the $J=0$ bound exciton state. This interpretation requires a large exchange splitting of $\Delta_{JJ}=90$ meV. A J-J coupling of this size implies an unusual degree of overlap and therefore a strong exchange interaction between the electron and hole of the bound exciton. The COL centre which is a triple Cu associate similarly shows an unusually large exchange splitting [11]. In agreement with the increased binding energy of the 1.911 eV centre compared with the COL, and hence generally more localized wavefunctions, the exchange splitting is larger for the former ($\Delta_{JJ}=90$ meV for the 1.911 eV centre but $\Delta_{JJ}=23.2$ meV for the COL).

Cu is known to create deep acceptor states in GaP, 0.5 and 0.7 eV from the valence band edge [4]. The centres causing the acceptor levels are not identified, but presumably Cu_{Ga} is involved in complexes with other defects. Hence, it may be concluded that the hole is also very tightly bound to the isoelectronic centre suggested here if the hole wavefunction is mainly localized on an acceptorlike associate containing Cu_{Ga} (e.g. the $(\text{Cu-Ga})_{\text{Ga}}$ split interstitial). An interstitial Cu_{I} as the donor part also binds the electron rather tightly, probably ≥ 100 meV. The localization energy of the bound exciton formed by the two particles is then reduced to the observed 0.4 meV mainly through Coulomb repulsion. The BE states involved are deep compared to effective mass theory and the

exciton must be very localized at the defect. Also as discussed above, the hole states are strongly perturbed by the local axial field compared with the host states. It might therefore be argued that a description of an exciton of a Frenkel type as a local excitation of the defect is appropriate in this case. The direct local BE excitation might be viewed as a charge transfer process, where an electron is transferred from the acceptor-like part of the complex to the donor-like part. In the model discussed above the parts are the $(\text{Cu-Ga})_{\text{Ga}}$ split interstitial acceptor and the Cu_{I} donor. One reasonable interpretation of the thermal activation energy $E_1 = 120 \text{ meV}$ (Fig. 6) in this picture of the 1.911 eV emission is that it corresponds to the binding energy of the less tightly bound electron. The quenching of the emission occurs upon release of the electron after thermal excitation. At high temperatures this process is competing with relaxation to the lowest BE state.

The electronic line C_0 , 280 meV above the 1.911 eV transition is attributed to transitions to bound exciton states derived from the $p_{\pm}$ split-off hole states (Fig. 16). This gives roughly the size of the axial field splitting, neglecting Δ_{SO} . A lifetime broadening of the C_0 component is consistent with rapid excitation transfer to lower bound exciton states or to continuum states where one particle is ionized. The A_0 line is also lifetime broadened, though to a lesser extent. At this point the details of the higher energy components are not firmly established. The level scheme presented, however, accounts for the properties of the 1.911 eV bound exciton, consistent with the identification of the centre binding the exciton as being a linear $\langle 100 \rangle$ -oriented defect.

VII. Conclusions

The BE emission bands introduced into GaP upon Cu diffusion under proper conditions are the subject of a systematic optical study, including the investigations of the 1.911 eV bound exciton reported here. Together with the COL bound exciton at 2.1774 eV, the 1.911 eV BE exhibits several unusual properties, which seem to be characteristic for excitons bound to Cu-complexes in GaP [11,19,30]. The 1.911 eV BE emission is observed only after Cu-diffusion at high temperatures, about 1050 °C, when the temperature is rapidly quenched after a typical diffusion time of about 1 hr. Attempts to relate this BE to any other dopants have failed as also observed in previous doping experiments [8,22]. The presence of Cu in the defect complex is therefore concluded from the doping procedure as well as isotope shifts of some phonon replicas when substituting Cu⁶³ for Cu⁶⁵. The absence of isotope shift for the dominating 10 meV phonon replica in the emission spectrum on the other hand suggests that other species besides Cu are also involved. In view of the doping results Ga_I is proposed as the additional part of the associate. In agreement with the defect symmetry determined from ODMR measurements it is concluded that the linear <100>-oriented (Cu-Ga)_{Ga} split interstitial is likely to be responsible for the 1.911 eV emission, either as a neutral associate with an unfilled d-shell or paired with a Cu_I donor as an isoelectronic molecule. Both defects are consistent with the fact that two electrons are needed to compensate Cu_{Ga} when forming a neutral centre. However the very long decay time indicating the absence of Auger effects and hence, no spin in the final state of the recombination seems to favour the latter alternative. A defect with an open d-shell would also be expected to be depending on the shallow doping for the right charge state, which is not the case for the suggested associate.

A consistent theory for bound excitons is in an early state of development and hence, a tentative model for the complex states of the 1.911 eV BE based on experimental results is provided in this paper. It is argued that the combination of a dominant axial field of compressional sign and an extraordinarily large exchange interaction explains the electronic structure of the bound exciton. The lowest electron states in this case are a singlet-triplet pair. A spin selection rule stating that a transition between a pure spin triplet state and a singlet is forbidden is indicated in the PLE spectrum. There the $J=0$ line at 2.002 eV has much larger oscillator strength than the 1.911 eV line has. This selection rule is similarly manifested for the COL centre [11].

In conclusion, the suggested level scheme and the identification of the 1.911 eV centre account for the observed properties of the exciton bound to this centre. A theoretical model is needed relating the binding energies to the vibrational properties for the two excitons bound to Cu complexes in GaP discussed above, the more deeply bound 1.911 eV BE showing a weaker phonon coupling than the more weakly bound COL exciton.

References

1. See e.g. H.J. Queisser, Solid State Electronics 21, 1405 (1978) and references therein
2. A.G. Milnes, Deep Impurities in Semiconductors (Wiley, New York, 1973) p. 16
3. F. Willman, D. Bimberg and M. Blätke, Phys. Rev. B 7, 2473 (1973)
4. H.G. Grimmeiss, B. Monemar and L. Samuelson, Solid State Electronics 21, 1505 (1978).
5. A.A. Bergh and P.J. Dean, Light Emitting Diodes (Clarendon Press, Oxford, 1976)
6. F.A. Kröger, The Chemistry of Imperfect Crystals (North Holland Publishing Company, Amsterdam, 1964)
7. J.A. Van Vechten in Handbook of Semiconductors, Vol. 3, Materials, Properties and Preparation, Ed. S.P. Keller (North Holland, Amsterdam, 1980) Ch. 1
8. P.J. Dean, J. Luminescence 7, 51 (1973)
9. D.V. Lang, J. Appl. Phys. 45, 3023 (1974)
10. J.A. Van Vechten, C.M. Ransom and T.J. Chappell, Proc. 15th Int. Conf. Physics of Semiconductors (Kyoto, 1980), J. Phys. Soc. Japan 49, Suppl. A 251 (1980)
11. B. Monemar, H.P. Gislason, P.J. Dean and D.C. Herbert, unpublished
12. S. Depinna, B.C. Cavenett, N. Killoran and B. Monemar, unpublished
13. M.D. Sturge, E. Cohen and K.F. Rodgers, Phys. Rev. B 15, 3169 (1977)
14. T.N. Morgan, B. Welber and R.N. Bhargava, Phys. Rev. 166, 751 (1968)
15. C.H. Henry, P.J. Dean and J.D. Cuthbert, Phys. Rev. 166, 754 (1968)
16. J.J. Hopfield, D.G. Thomas and R.T. Lynch, Phys. Rev. Lett. 17, 312 (1966)
17. P.J. Dean and D.C. Herbert, in Topics in Current Physics, Vol. 14, Ed. K. Cho (Springer Verlag, Berlin, 1979) p. 55

18. B.C. Cavenett, *Advances in Physics*, to be published
19. H.P. Gislason, B. Monemar, P-O. Holtz, P.J. Dean and D.C. Herbert, unpublished
20. R.N. Bhargava, S.K. Kurtz, A.T. Vink and R.C. Peters, *Phys. Rev. Lett.* 27, 183 (1971)
21. P.J. Dean, *Solid State Commun.* 9, 2211 (1971)
22. D.R. Wight, J.W.A. Trussler and W. Harding, *Proc. XIth Conf. on Semiconductors* (Warsaw, 1972) p. 1091
23. B. Monemar, H.P. Gislason, P.J. Dean, S. Depinna and B.C. Cavenett, unpublished
24. P.J. Dean, *Phys. Rev. B* 4, 2596 (1971)
25. A.A. Maradudin in *Solid State Physics*, Vol. 18, Ed. F. Seitz and D. Turnbull (Academic Press, New York, 1966) p. 273
26. J.L. Yarnell, J.L. Warren, R.G. Wenzel and P.J. Dean, *Neutron Inelastic Scattering* 1, 301 (1968)
27. K.M. Lee, Le Si Dang, G.D. Watkins and W.J. Choyke, *Solid State Commun.* 37, 551 (1981)
28. K. Morigaki, P. Dawson and B.C. Cavenett, *Solid State Commun.* 28, 829 (1978)
29. T.N. Morgan, *Phys. Rev. Lett.* 21, 819 (1968)
30. P.J. Dean, B. Monemar, H.P. Gislason and D.C. Herbert, *Proceedings of the 1981 ICL, Berlin*, to be published in *J. Luminescence*
31. D.J. Robbins and P.J. Dean, *Advances in Physics* 27, 499 (1978)
32. J.W. Corbett and J.C. Bourgoin in *Point Defects in Solids*, Vol. 2, Ed. J.H. Crawford, Jr. and L.M. Slifkin (Plenum Press, New York, 1975) Ch. 1
33. P.J. Dean, W. Schairer, M. Lorenz and T.N. Morgan, *J. Luminescence* 9, 343 (1974)

34. P.J. Dean, R.A. Faulkner, S. Kimura and M. Illegems, Phys. Rev. B 4, 1926 (1971)
35. D.J. Robbins, D.C. Herbert and P.J. Dean, J. Phys. C 14, 2859 (1981)

Table I

Phonon energies from the sideband of the 1.911 eV luminescence spectrum in Fig. 2

Notation	Phonon energy meV	ΔE ($\text{Cu}^{63}\text{-Cu}^{65}$) meV	Interpretation
B_1	10.3	0	
B_2	12.4	0	
B_3	15.4	0.2	
B_4	20.9	0.2	
$2B_1$	22.0		Second replica of B_1
B_5	24.2	0.5	Distorted LA mode
B_6	26.9	0.3	
$3B_1(B_7)$	34.8	0	Third replica of B_1
B_8	37.4	0	Local gap mode
B_9	39.9	0.1	Local gap mode
B_{10}	42.5	0	
B_{11}	55.7		

Table II

Energies of the observed structure in the PLE spectrum of the 1.911 eV emission in Fig. 7

Notation	Photon energy	Phonon energy	Interpretation
B_0	1.911 eV		J=1 BE triplet
A_0	2.002 eV		J=0 BE singlet
A_δ		3.8	Quasilocalized low energy mode
A_1		10.2	cf. B_1 in Fig. 2
$2A_1$		21	Second B_1 replica
$3A_1$		33	Third B_1 replica
A_8		34.8	cf. B_8 in Fig. 2
A_9		38.7	cf. B_9 in Fig. 2
A_{10}		42.5	cf. B_{10} in Fig. 2
C_0	2.1928 eV		Electronic transition to BE states from split off hole states (see Fig. 16)
C_1		16.8	Phonon replica of C_0
C_2		34	Local gap mode of C_0
C_3		37.2	Local gap mode of C_0

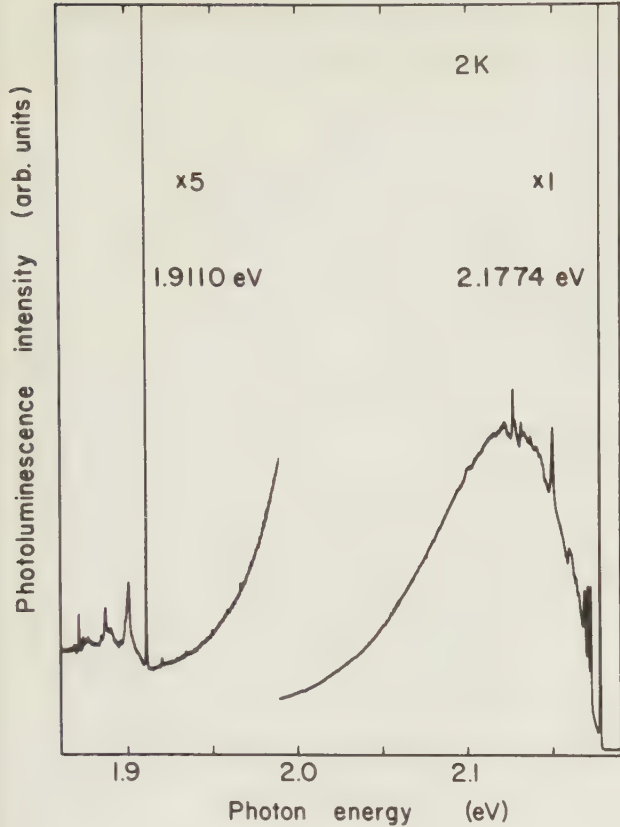
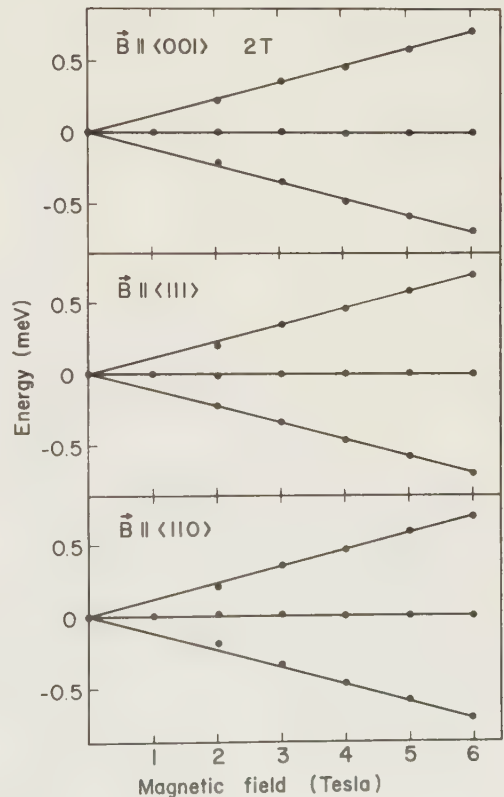
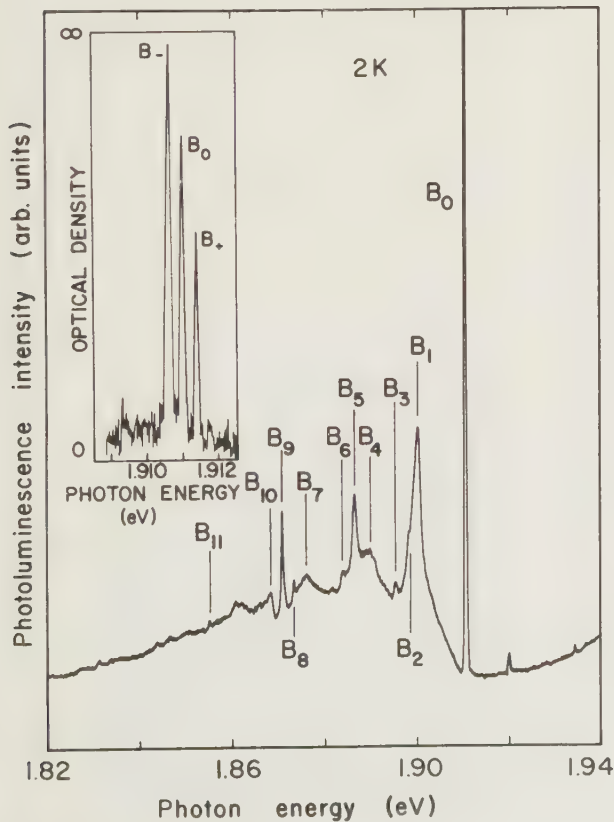


Fig. 1. The two dominant bound exciton PL bands typical of GaP diffused with Cu at 1050 °C, recorded at 1.8 K. The emission at higher photon energy is the so called COL bound exciton emission with lowest electronic line at 2.1774 eV. The intensity of the low energy spectrum with electronic line at 1.911 eV is uncorrelated to the intensity of the COL emission. Sometimes this spectrum is absent indicating a more critical doping procedure.

Fig. 2. PL spectrum of the 1.911 eV BE emission for the same sample as in Fig. 1, recorded at 2 K. The excitation wavelength is 5145 Å (to the left, below). In the inset is shown the splitting of the 1.911 eV line into three components in magnetic field $B=3.4$ T, $B//\langle 100 \rangle$. The splitting is nearly isotropic as shown for $B//\langle 001 \rangle$, $B//\langle 111 \rangle$ and $B//\langle 110 \rangle$ (to the right).



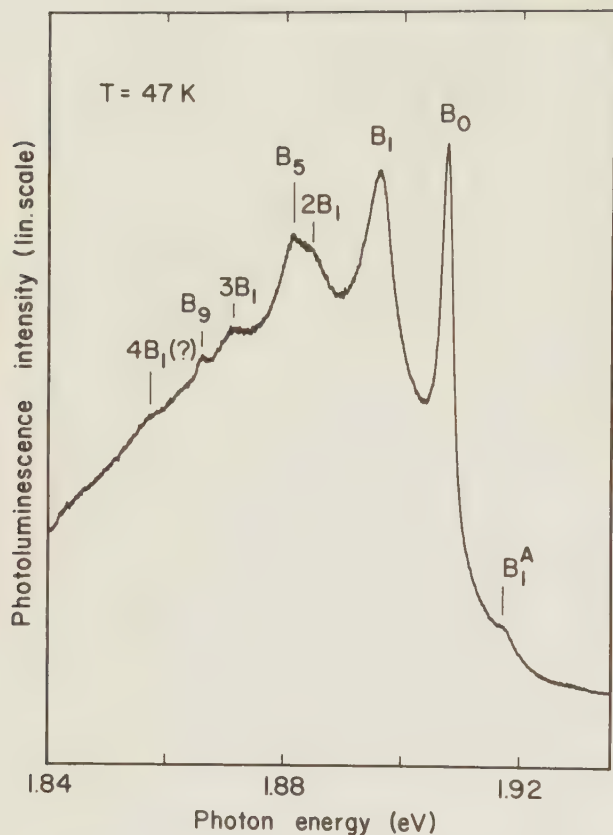


Fig. 3. Portion of the PL spectrum for the same crystal as in Fig. 2, recorded at 47 K. An anti-Stokes component of the phonon mode B_1 about 9 meV above the reduced no-phonon line first appears at 25 K. The phonon energy in the excited vibronic state is reduced by about 10 % compared with the ground state.

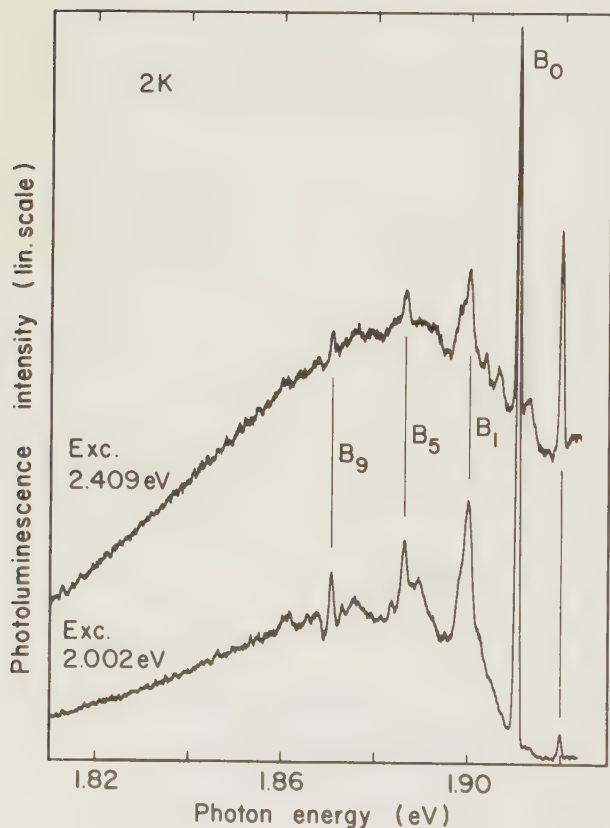


Fig. 4. PL spectrum for a Cu-diffused GaP sample, different from the one in Figs. 1 and 2. The upper curve shows a transition at 1.9202 eV, which is strong in this sample, when excited above the bandgap at 5145 Å. The phonon replicas of this line dominate the phonon sideband, which is very different from the sideband in Fig. 2. When exciting with a cw dye laser in the strong 2.002 eV absorption line observed in PLE, only the 1.911 eV line and its phonon replicas are enhanced, giving the familiar spectral shape shown in the lower curve.

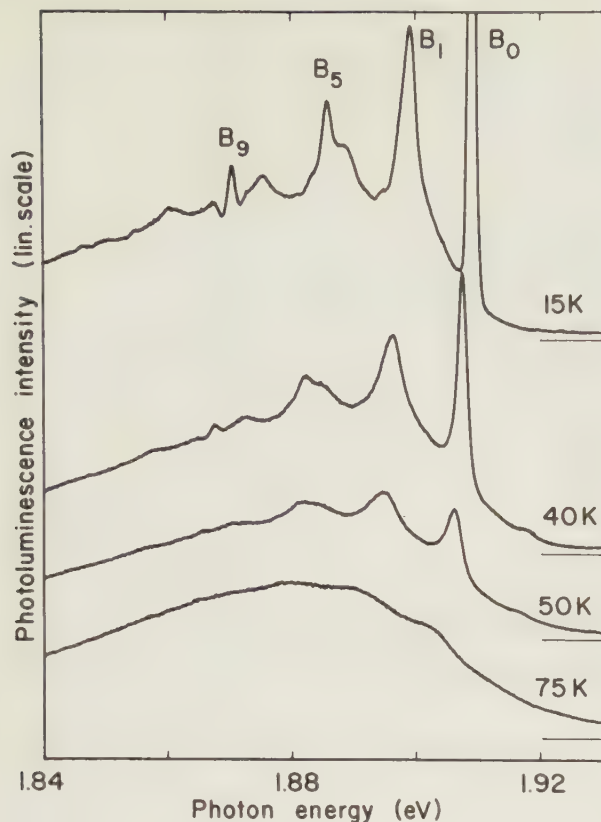


Fig. 5. The spectral evolution of the 1.911 eV emission band with rising temperature. The electronic line is visible up to about 100 K, where all structure vanishes, although it is very much smeared out above 80 K. At elevated temperature the phonon side-band clearly consists of replicas of the electronic line with a dominating 10 meV phonon mode. This same mode is also observed on the anti-Stokes wing. The total intensity of the emission is not affected much until above 80 K.

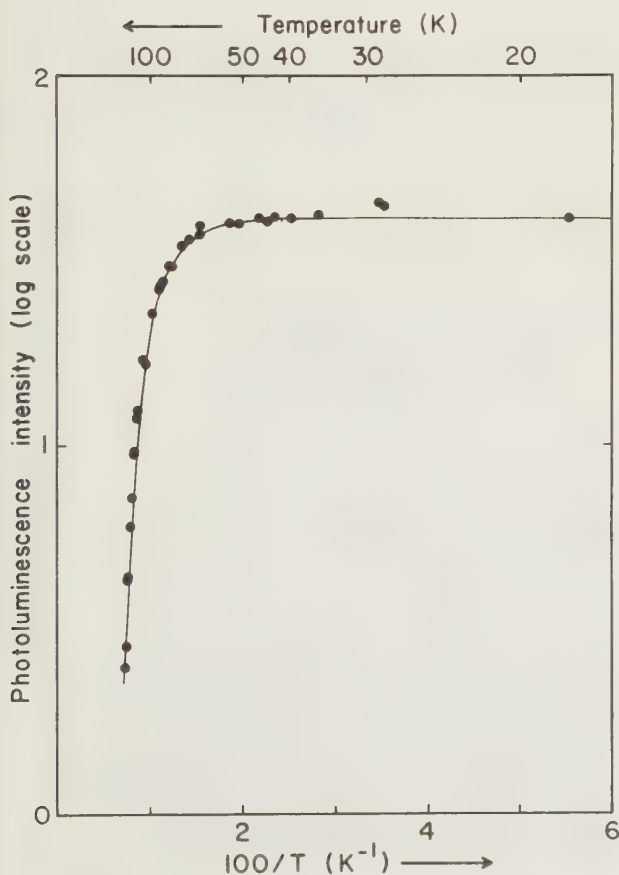


Fig. 6. Temperature dependence of the total emission intensity for the 1.911 eV emission taken with extrinsic excitation at 2.03 eV. The thermal activation energy as the emission rapidly disappears in the temperature range 100-130 K is $E_1 = 120 \pm 10$ meV. The smaller decrease before the final step corresponds to a second activation energy $E_2 = 30 \pm 5$ meV.

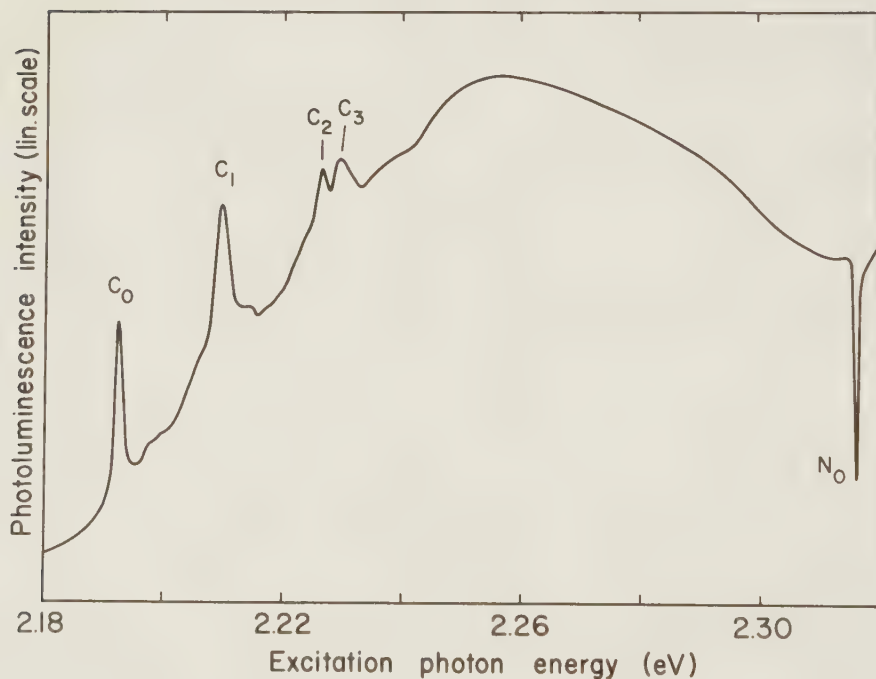
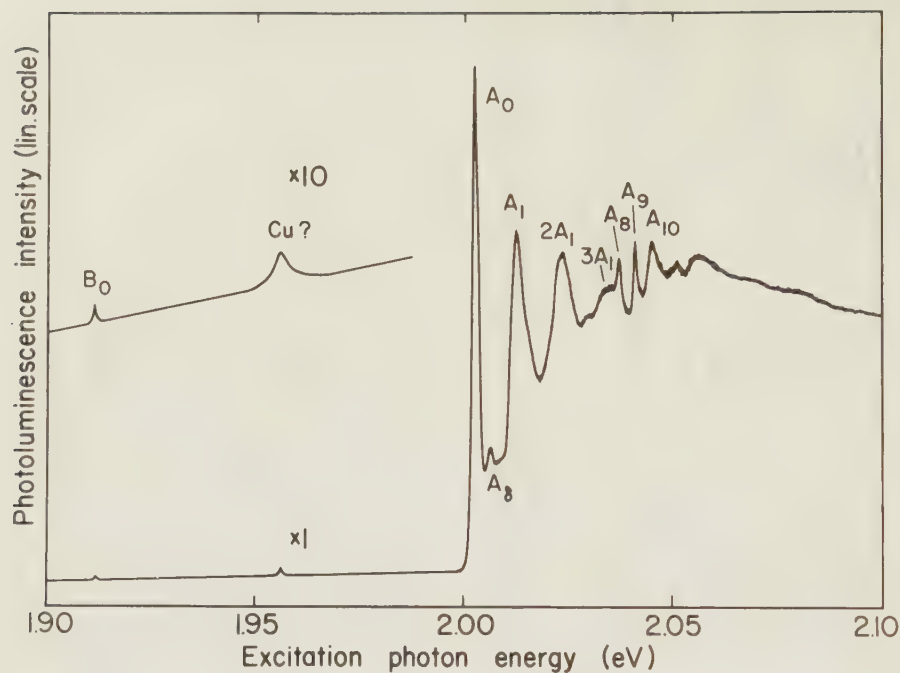


Fig. 7. A PLE spectrum for the 1.911 eV emission obtained with a tuneable cw dye laser at 1.8 K. The detection wavelength is 6550 Å or 6650 Å alternatively. The electronic line B_0 at 1.911 eV is a spin forbidden triplet transition, just barely detectable. The strong phonon wing above the electronic line A_0 at 2.002 eV shows general similarities in phonon coupling as observed for the B_0 emission line at 1.911 eV. A_0 is attributed to a $J=0$ singlet BE state and the replicas A_1 - A_7 are manifestations of the same 10 meV phonon mode as in the emission spectrum in Fig. 2. The C_0 line is discussed in the text.

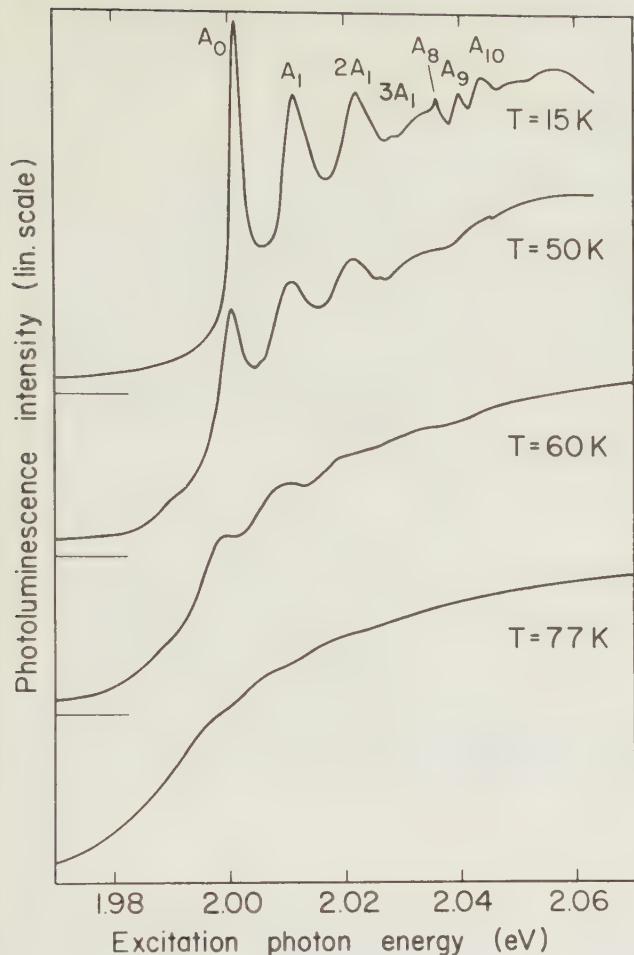


Fig. 8. Portions of PLE spectra for the 1.911 eV emission at several different temperatures. The spectral evolution of the structured absorption band when the temperature is raised is largely similar to the case of emission in Fig. 6. Thus the dominant 10 meV phonon mode is clearly seen at elevated temperatures both on the Stokes and the anti-Stokes wing.

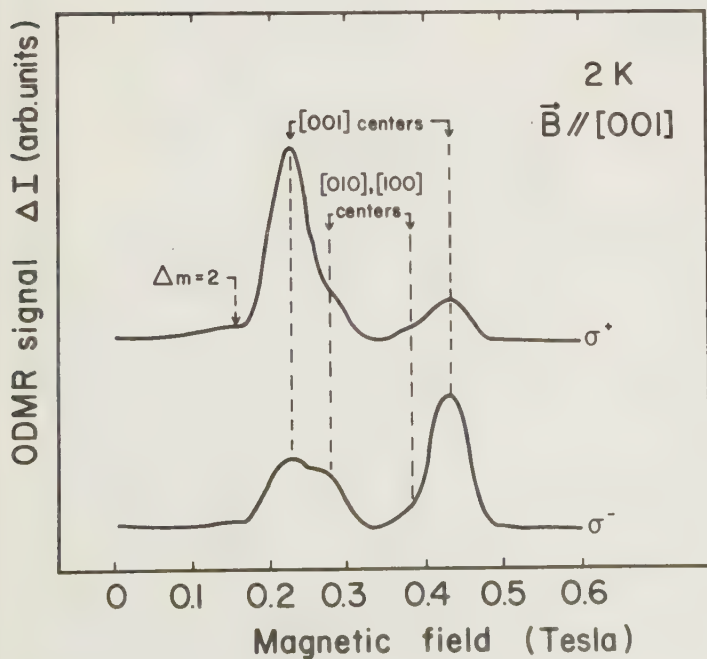


Fig. 9. ODMR signals for $\vec{B} // [001]$ obtained by monitoring $\Delta I_{\sigma+}$ (upper curve) and $\Delta I_{\sigma-}$ (lower curve). The spectrum consists of $\Delta M_S = \pm 1$ resonances from the three centres [001], [010] and [100] as shown and a single $\Delta M_S = \pm 2$ resonance which is approximately the same for each centre.

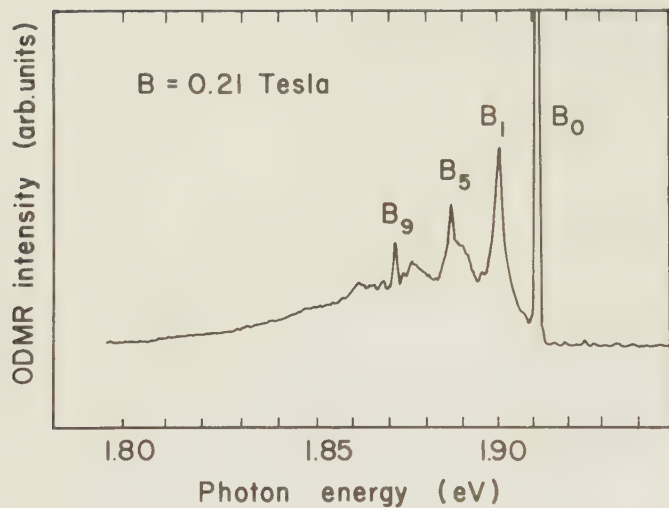


Fig. 10. Spectral dependence of the ODMR triplet resonance at high resolution (0.1 nm).

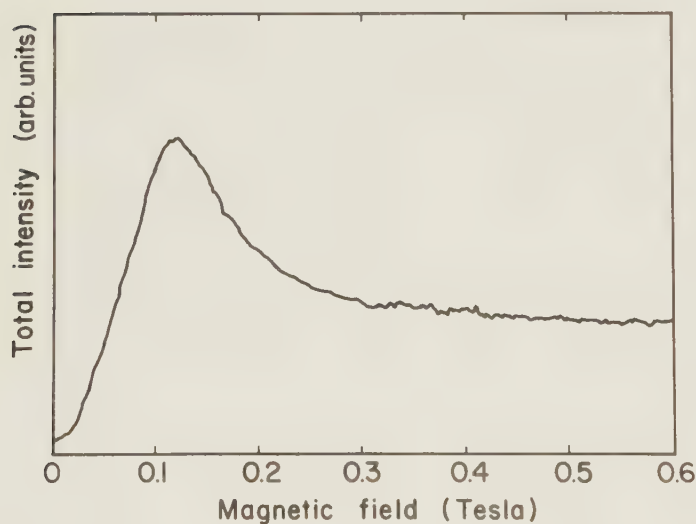
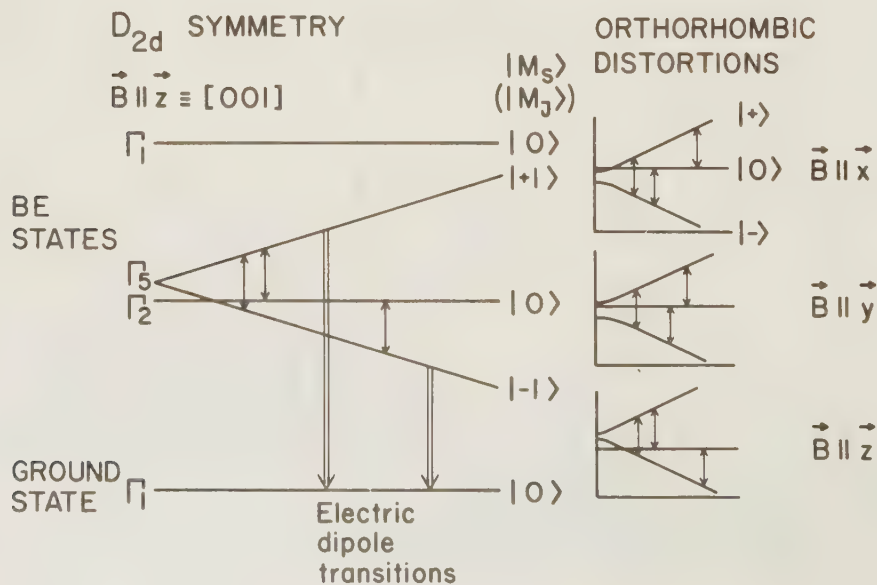


Fig. 11. Level crossing signal (ΔI vs B) for $\vec{B} // [001]$ monitoring all of the $I_{\sigma+}$ emission.



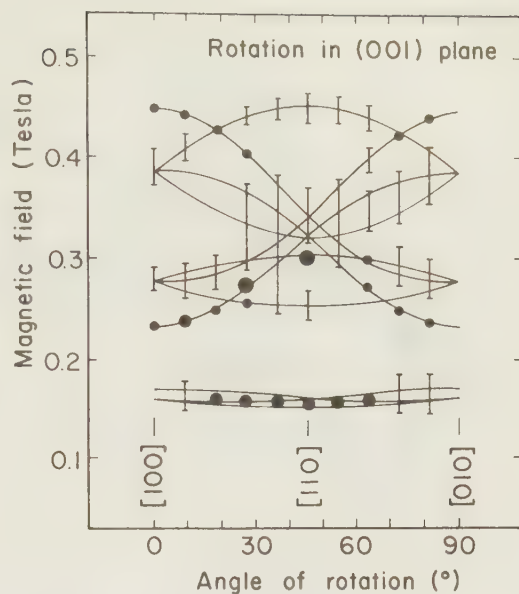
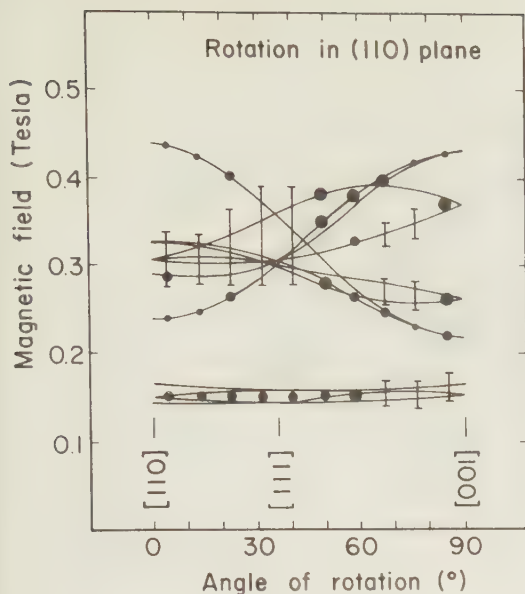


Fig. 13. Angular dependence of the triplet ODMR spectrum for rotation in the (110) plane and the (001) plane. The solid lines are calculated for orthorhombic symmetry with the parameters given in the text.

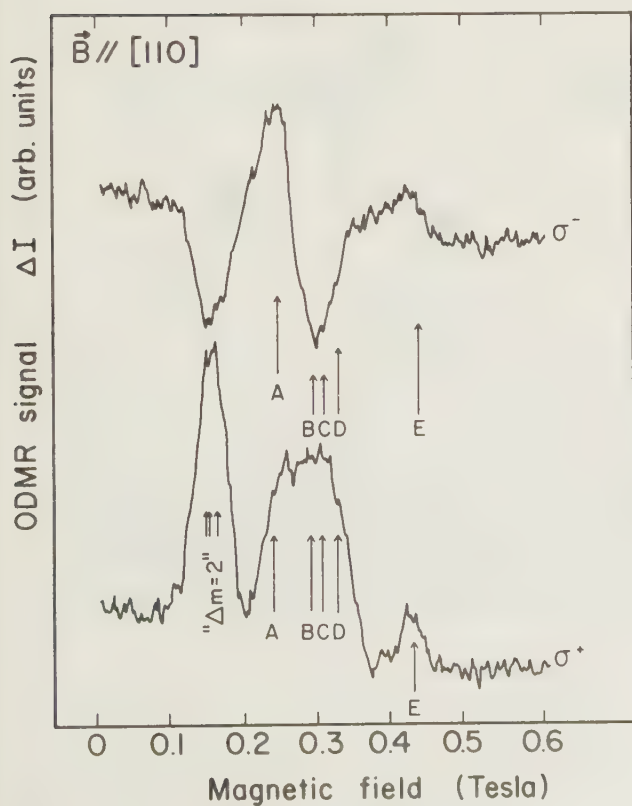


Fig. 14. An ODMR spectrum for $\vec{B} // [110]$. When the magnetic field orientation is away from the defect axis (the z-direction) emission is allowed for all levels in Fig. 13 and population differences are small. Then all resonances are weak.

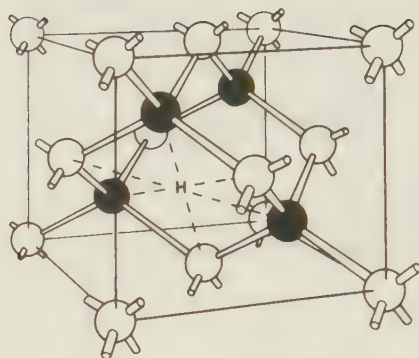
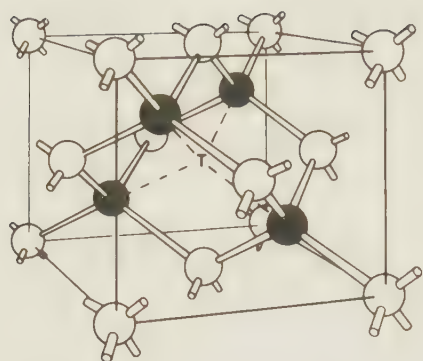


Fig. 15a. The two different types of interstitial sites in the zincblende lattice. There are two inequivalent tetrahedral sites (T). In GaP one is surrounded by Ga atoms and the other by P atoms. This type of interstitial sites is shown to the left in the figure. To the right a hexagonal site (H). This interstitial site is at the midpoint between two inequivalent T sites along the $\langle 111 \rangle$ axis.

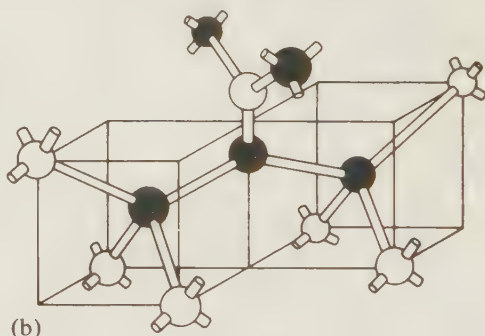
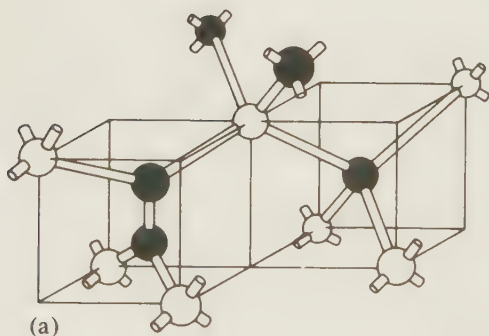


Fig. 15b. Possible configurations of a split - $\langle 100 \rangle$ interstitial in the zincblende lattice. In GaP either two Ga atoms or two P atoms can occupy the same substitutional site, as shown to the left, or a pair of different atoms forms a mixed split interstitial, as shown to the right (a Ga atom and a P atom). Note that each atom of the split interstitial pair has only three bonds.

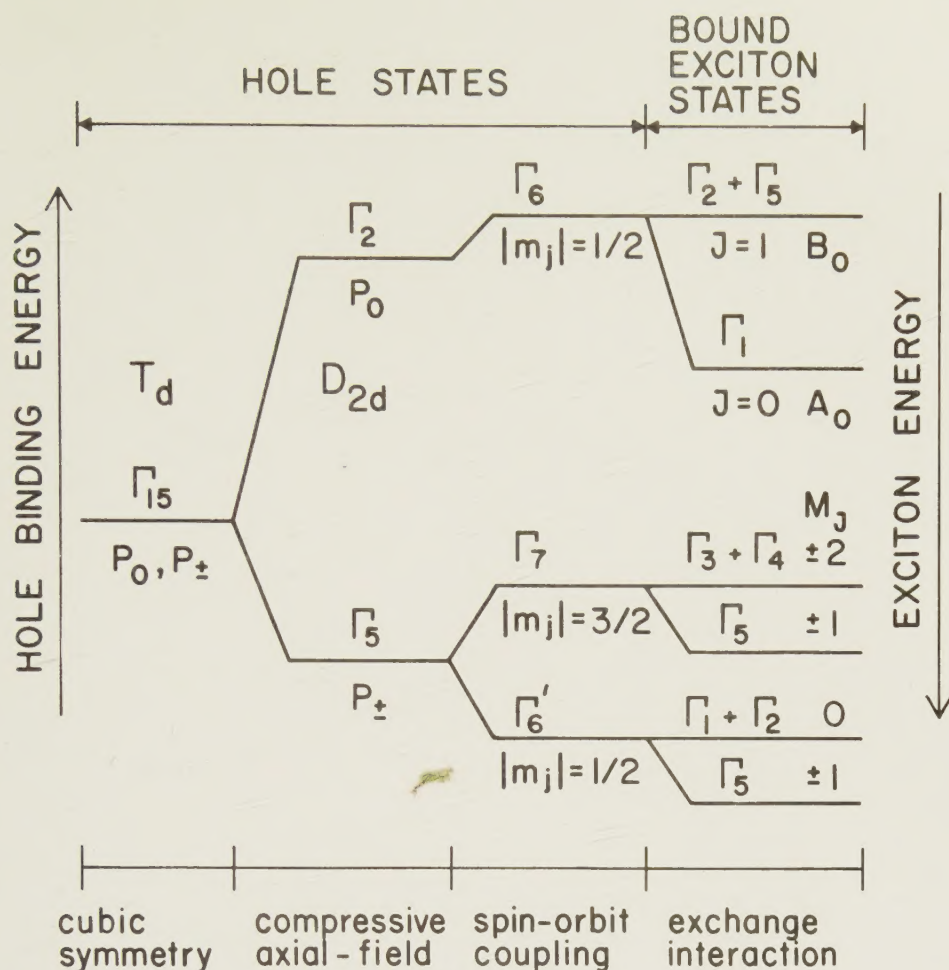


Fig. 16. Level diagram for the 1.911 eV bound exciton. To the left hole states are shown to split from the triply degenerate Γ_{15} representation into a p_0 singlet hole state (at highest hole binding energy for compressive strain field) and a doubly degenerate $p_{\pm}$ hole state. Adding the smaller spin-orbit coupling a pure spin state Γ_6 has the highest hole binding energy while the $p_{\pm}$ state splits into Γ_6' and Γ_7' doublets. To the right the bound exciton states are shown. The combination of two pure spin particles gives a singlet-triplet pair $J=0,1$ where the triplet is the lowest BE state. The observed energy differences obtained from Fig. 7 are indicated in the diagram. The 1.911 eV transition is between the spin forbidden triplet $J=1$ (highest in the diagram) and the spin free ground state.

